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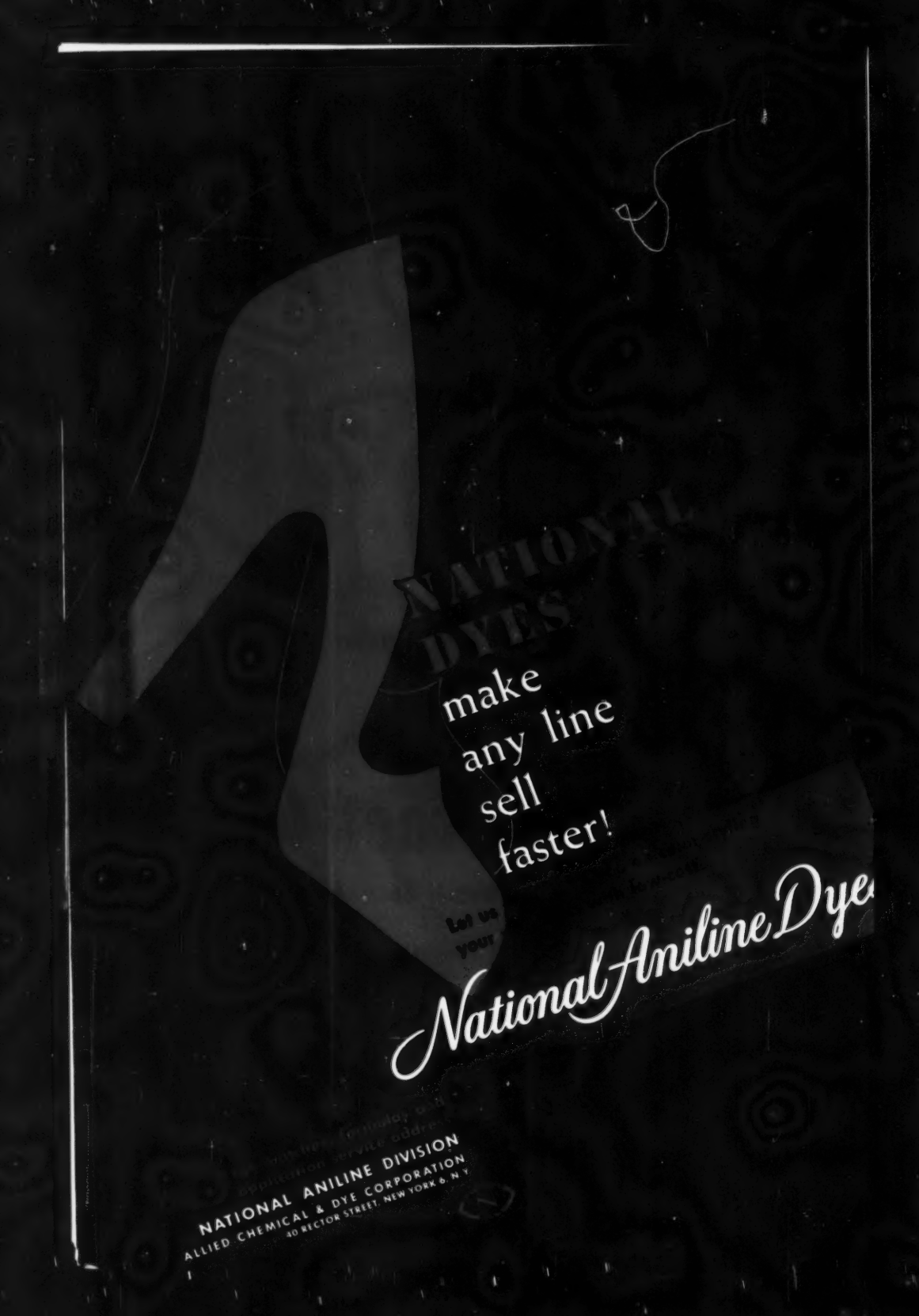
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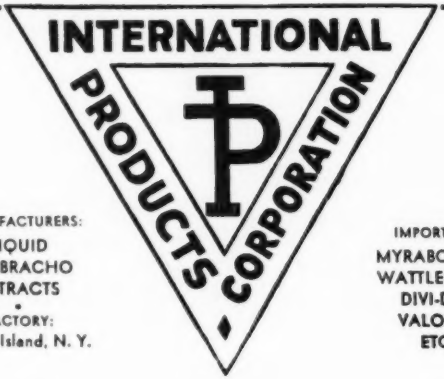

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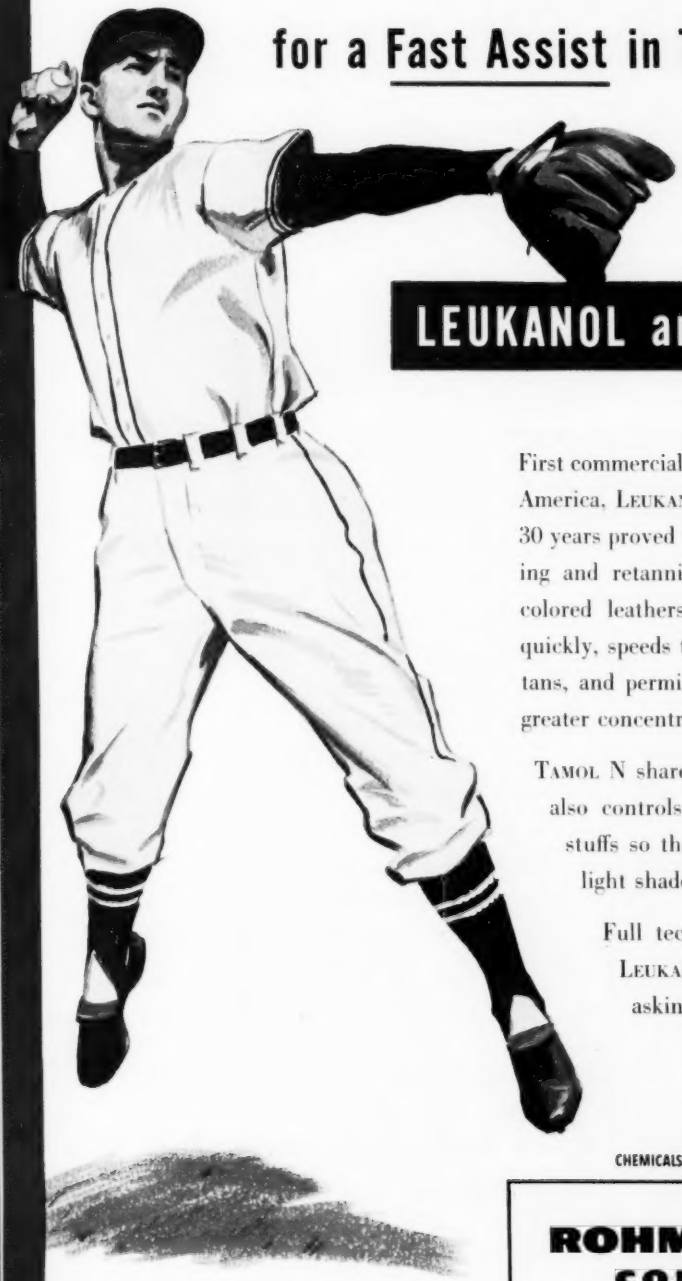

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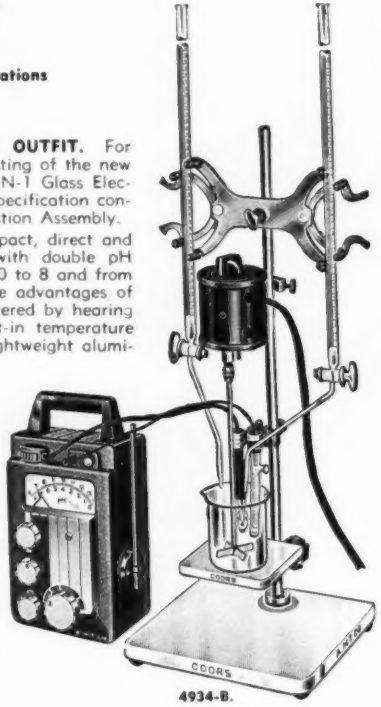

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Study of Leather Pasting

III. Some Notes on Fatliquor–Adhesion Relationship

By WILLIAM R. COX*

Department of Basic Science in Tanning Research
Foundation Tanners' Council of America
University of Cincinnati

INTRODUCTION

Earlier studies[1] of the mechanism of the "pasting" process for drying leather considered some of the conditions which are necessary for satisfactory results. When the dry leather is removed from the pasting plate the strength of the bonds between the adhesive film and the leather surface, as well as between the adhesive film and the plate surface are important. Best results are usually obtained when there is a fairly strong bond between the plate surface and the adhesive film, coupled with a relatively weak bond between the leather surface and the pasting plate. When these conditions are satisfied

*Former member of staff.

the leather will strip cleanly leaving the majority of the adhesive on the plate surface.

Previous research on the paste-drying process indicated that the type and amount of fat or oil in or on the grain surface of the leather profoundly affected its pasting character. Because of these results we undertook a preliminary study of the fatliquoring operation (which adds this fat to the leather) as it affects the dry adhesive character of the leather.

Experimental

Chrome tanned calfskin shoulders were used in all of the work to be reported. The stock was prepared in the tannery, vegetable mordanted, and acid dyed before shipment to the laboratory in the wet state ready for fatliquor. The various lots used contained from 4.45 to 4.65 per cent chrome oxide on the hide substance basis.

Upon receipt of the leathers at the laboratory, groups consisting of eight pieces each measuring approximately 4 inches by 6 inches were prepared for fatliquoring experiments. In selecting samples for the different groups we used only the center portions of the shoulders, and each group was systematically randomized among the various shoulders represented by the particular lot in use. These precautions insured that each group of samples represented the various areas and shoulders in the lot. After grouping, the samples were sealed in moisture-proof bags, quick frozen at minus 20°F. and stored in a "deep freezer" at minus 10°F. until used. Preliminary experiments demonstrated that such samples may be stored for periods up to 30 days without affecting the results.

The fatliquoring procedure employed followed that of Koppenhoefer and Retzsch [2] with some modifications. For a fatliquoring experiment the samples were removed from the freezer and allowed to thaw overnight at laboratory temperature. The next morning the samples were washed in 500 ml. of distilled water for twenty minutes at 120°F. The washing and subsequent fatliquoring operations were carried out in two liter bottles which were rotated continuously in a Launderometer.

After washing, the samples were drained, lightly squeezed, and weighed. All fatliquor percentages employed were calculated on the washed and drained weight of the leather. The samples were then transferred to the fatliquor emulsions which had been previously heated to 120°F. and fatliquored for one hour at that temperature. The fatliquor emulsions employed will be described later.

After fatliquoring the pieces were drained and wrapped in aluminum foil overnight to exclude air from the leather and simulate the "horsing up" operation of the tanner. The next morning 16 one by two inch pieces were cut from each experiment, the remainder of the leather being reserved for subsequent chemical analysis. These pieces were paste-dryed in contact

with glass plates and the dry adhesion determined by means of previously described methods [3]. A three per cent potato starch paste was used.

Preliminary experiments showed very wide variations in the results unless a reproducible method for preparing the fatliquor emulsions was rigidly adhered to. In order to minimize this effect the following procedure was employed in all of the work reported here. The calculated quantity of oils were weighed into a 50 ml. beaker, and distilled water at 120°F. was added with constant stirring until the volume was twice that of the original oils. Care was taken to scrape all of the adhering oils from the side and bottom of the beaker with a rubber "policeman". This concentrated emulsion was poured rapidly with constant stirring into the required volume of water at 120°F. The final liquid volume was in all cases equal to twice the drained weight of the leather samples.

Chemical Analysis

The total leather as well as the grain area of most fatliquoring experiments was analyzed for fat, hide substance, and moisture, according to methods similar to those employed in the second paper of this series. A single ethyl ether extraction was used, however, for the fat determinations. No analytical data is given for the top-fatliquoring experiments. These data are presented as a function of per cent fatliquor given to the leather.

The quantity of oil present in the special fatliquor emulsions was determined by means of a modification of the Babcock butterfat test for milk [4]. From this value, the percentage take-up of oil by the leather was calculated.

Results and Discussion

A commercially prepared sulfated neatsfoot oil was used in the work reported here. The analysis of the batch of oil is presented in Table I. A supply of the oil was fractionated using a method supplied by Koppenhoefer [5], and the effect of sulfo oil fraction used alone as a fatliquor was studied. In addition, the effect of adding various quantities of raw neatsfoot oil and of a U.S.P. mineral oil to the intact sulfated oil was studied. Finally some preliminary top fatliquoring experiments were carried out.

TABLE I

Analysis of Sulfated Neatsfoot Oil

Constituent	Per Cent
Fatty Acids as Soaps	2.6
Free Fatty Acid	15.7
Sulfo Oleic Acid	15.1
Total Fatty Matter	66.7
Neutral Oil	35.9
Unsaponifiable Matter	0.6
Moisture	22.7

The Sulfo Oil Fraction

The work of Koppenhoefer and Retzsch [6] showed that the sulfo oil fraction of a sulfated oil functions only as the emulsifier furnishing no lubrication to the leather. In Table II are presented the analyses and the dry adhesion of leathers fatliquored with up to 12 per cent of the sulfo oil fraction.

TABLE II

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—Sulfo-Oil Fraction from Medium Sulfated Neatsfoot Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	86.7	0.58	74.8	5.3	1520
5.51	76.6	3.80	56.2	12.9	1395
8.46	73.9	4.57	56.5	10.6	1360
12.46	69.7	7.68	57.4	9.7	1500

The following discussion will give physical meaning to the data presented in Table I and in the tables and figures to follow. Under the experimental conditions employed in the laboratory, leather sample must show an average adhesion of approximately 450 grams or less before all tendency toward sticking and grain damage is eliminated.

When we apply this yardstick to the data of Table I it is seen that grain damage was encountered at all levels of the sulfo oil fraction employed. As the quantity of sulfo oil was increased only an insignificant decrease in the high adhesion of the leather took place. It can be concluded that the sulfo oil fraction when used alone has little or no effect on the adhesion of the leather.

The Effect of Adding Raw Neatsfoot Oil to the Intact Sulfated Oil

Studies of the effect of adding raw neatsfoot oil to the intact sulfated oil were carried out in four series of experiments. Fatliquor emulsions were prepared from the intact sulfated neatsfoot oil containing 0 per cent, 12½ per cent, 25 per cent, and 40 per cent of added raw neatsfoot oil on the dry basis. Leather samples were fatliquored with from one to four per cent of the above emulsions and the dry adhesion of the leather determined.

The results obtained are summarized in Tables III, IV, V, and VI. Presented in the tables are the dry adhesion of the leathers as well as the chemical analysis of the total sample and of the 100 micron split removed from the grain surface of the leather.

TABLE III

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—Sulfated Neatsfoot Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	87.2	1.84	76.2	4.9	1213
1.5	82.6	6.04	68.7	12.8	622
2.25	80.8	8.55	66.2	15.5	713
3.0	79.8	8.70	63.2	19.3	464
3.75	78.1	11.20	60.2	24.8	437

TABLE IV

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—87½% Sulfated Neatsfoot Oil—12½% Raw Neatsfoot Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	87.4	1.54	76.4	4.6	1244
0.77	84.4	3.40	72.6	7.65	994
1.55	83.2	5.77	67.9	12.65	694
2.32	81.9	7.43	64.5	17.1	662
3.10	80.9	8.91	64.1	18.3	544
3.88	78.0	11.65	60.0	24.7	744

TABLE V

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—75% Sulfated Neatsfoot Oil—25% Raw Neatsfoot Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	87.2	1.84	76.2	4.9	1213
1.0	81.6	4.46	71.8	7.5	410
2.0	78.3	7.48	65.8	14.65	462
4.0	73.3	13.70	59.8	22.7	276

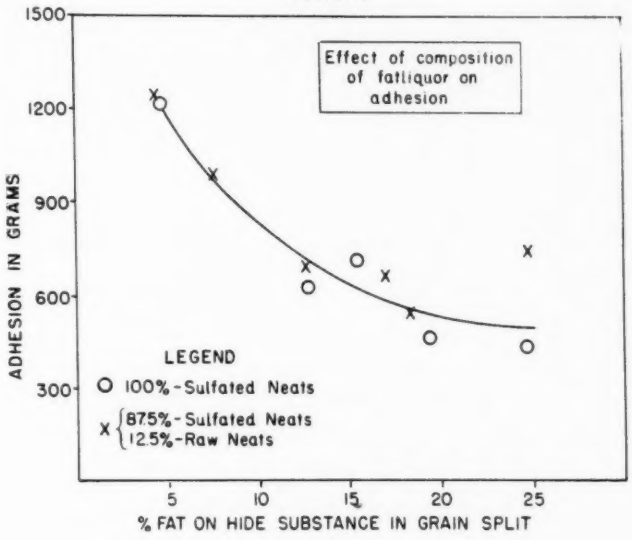
TABLE VI

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—60% Sulfated Neatsfoot Oil—40% Raw Neatsfoot Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	87.4	1.54	76.4	4.6	1244
1.0	82.0	4.81	71.9	6.9	462
2.0	80.2	7.41	66.6	14.1	267
4.0	74.7	13.20	60.2	23.7	208

Figure 1 is a plot of the adhesion results obtained using the sulfated neatsfoot oil alone, and the results obtained using a mixture of 87½ per cent of the sulfated neatsfoot oil and 12½ per cent of raw neatsfoot oil. The dry adhesion of the leather is plotted as a function of the per cent fat on the hide substance basis present in the grain split. Consideration of the curves of Figure 1 will show that the addition of 12½ per cent of raw neatsfoot oil to the fatliquor emulsion has effected little change in the adhesive character of the leather produced. All of the leathers showed considerable sticking and grain damage except at the highest fatliquor levels used.

FIGURE I



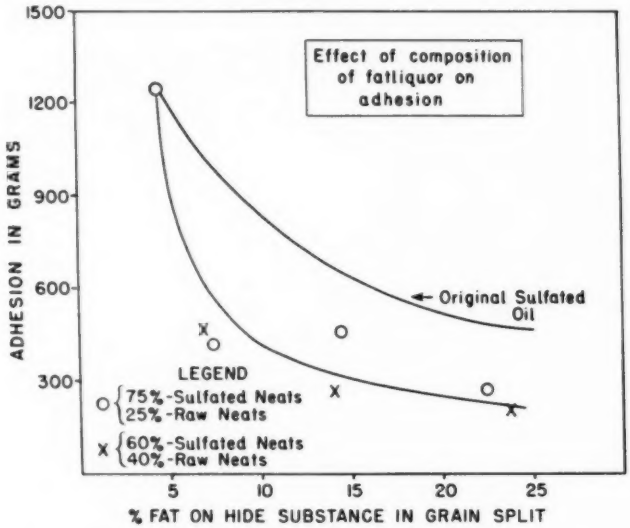
No explanation is offered for the seemingly unusually high adhesion obtained in one experiment with the sulfated oil-raw oil mixture. (Adhesion 744 grams with 24.7 per cent fat on hide substance basis in the grain split.) It must be emphasized again that carefully standardized laboratory conditions must be employed in order to obtain reproducible results. Even under these conditions erratic results are obtained on occasion.

In Figure 2 the results obtained when a mixture of 75 per cent sulfated neatsfoot oil and 25 per cent raw neatsfoot oil was used, as well as the results obtained using a mixture of 60 per cent sulfated neatsfoot oil and 40 per cent raw neatsfoot oil are summarized. As in Figure 1 the dry adhesion of the leather is plotted as a function of the per cent fat on the hide substance

basis present in the grain split. Included for comparison is the curve from Figure 1 giving the dry adhesion of the leather when the sulfated neatsfoot oil was used alone.

It is readily seen from the curves of Figure 2 that where either 25 per cent or 40 per cent of raw neatsfoot oil was added to the sulfated neatsfoot oil a leather of considerably lower adhesion was obtained. This was true of oil of the fatliquor levels employed. No difference was shown between the fatliquor containing 25 per cent of added raw neatsfoot oil and the fatliquor containing 40 per cent of added raw neatsfoot oil.

FIGURE 2



All of the adhesion values were in the vicinity of 450 grams or less. Sticking and damage to the grain surface of the leather did not occur when any of the samples from these two series were removed from the pasting plates. It is especially important to note that this was true even when only one per cent of fatliquor was employed.

The Effect of Adding Mineral Oil to the Intact Sulfated Oil

Because many fatliquors contain added mineral oils of one kind or another, the effect of adding mineral oil to the sulfated neatsfoot oil fatliquor was studied. A U.S.P. heavy mineral oil was used in the work to be reported here.

In two series of experiments, either 10 per cent or 25 per cent of the mineral oil was added to the intact sulfated neatsfoot oil and leathers fatliquored with from one to four per cent of these mixtures. The results obtained are summarized in Tables VII and VIII. Figure III is a plot of the adhesion data from Tables VII and VIII. As in the previous figures the dry adhesion of the leather is plotted as a function of the per cent fat on the hide substance basis present in the grain split. Included for comparison is the curve from Figure 1 giving the adhesion of the leather when the sulfated neatsfoot oil was used alone. When we examine Figure 3 we see that at low fat levels in the grain split the addition of the mineral oil to the fatliquor has not altered the adhesion of the leather. However, as we increase the amount of fat deposited in the grain split (by increasing the per cent fatliquor given to the leather) the mineral oil became more and more effective in reducing the adhesion of the leather. At higher fat levels in the grain split the adhesion values were the lowest recorded from any of the experiments. The data show no difference in the effect of using either, 10 per cent or 25 per cent of the mineral oil selected.

TABLE VII

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—90% Sulfated Neatsfoot Oil—10% U.S.P. Mineral Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	87.2	1.84	76.2	4.9	1213
1.0	86.2	4.14	71.1	9.7	871
2.0	83.6	7.08	65.8	15.4	456
4.0	80.1	12.2	59.9	23.0	247

TABLE VIII

Chemical Analysis and Dry Adhesion of Fatliquored Leather
Fatliquor Used—75% Sulfated Neatsfoot Oil—25% U.S.P. Mineral Oil

	Gross Leather		Grain Split		
% Fatliquor Given	% Hide Substance	% Fat on Hide Substance	% Hide Substance	% Fat on Hide Substance	Mean Adhesion Grams
0.0	87.4	1.54	76.4	4.6	1244
1.0	86.0	4.28	71.3	9.5	936
2.0	83.3	7.42	67.6	14.6	415
4.0	78.9	13.45	60.3	24.9	144

CONCLUSIONS AND SUMMARY

These preliminary laboratory studies were undertaken in order to demonstrate the effect of certain fatliquor components on the dry adhesion of pasted leather. The results indicate that the sulfo-oil fraction of a medium

FIGURE 3

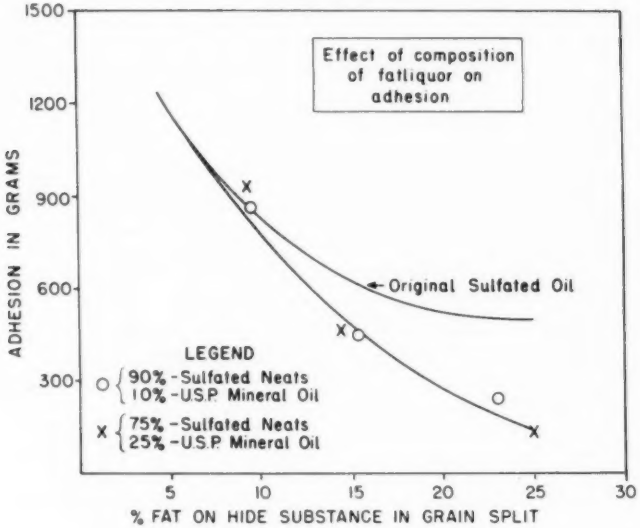
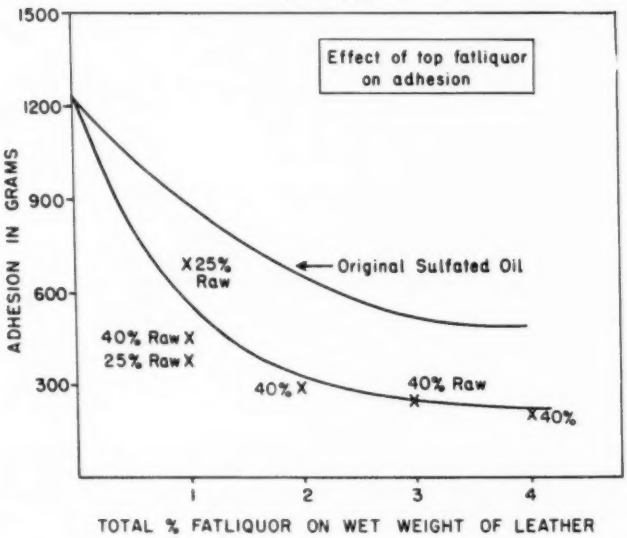


FIGURE 4



sulfated neatsfoot oil does not reduce the high dry adhesion of the unfatliquored leather. The sulfated neatsfoot oil alone yields a leather of satisfactory adhesion only at rather high fatliquor levels. By adding from 25 per cent to 40 per cent of raw neatsfoot oil to the sulfated neatsfoot oil fatliquor, leathers of satisfactory adhesion were obtained at low fatliquor levels. However, the addition of only 12½ per cent of the raw neatsfoot oil is completely without this effect.

The addtion of a U.S.P. heavy mineral oil to the sulfated neatsfoot oil seems to have a quantity effect. At the low fatliquor levels the mineral oil was without effect in reducing the adhesion of the leather, but as larger quantities of fatliquor were fed to the leather the effect of the mineral oil was more and more pronounced. At high fatliquor levels leathers were obtained which adhered very loosely to the pasting plates.

The studies were extended to include some top fatliquoring experiments. A one per cent top fatliquor consisting of the sulfated neatsfoot oil containing either 25 per cent or 40 per cent of added raw neatsfoot oil produced a leather of satisfactory adhesion at fairly low total fatliquor levels.

The present work demonstrated the wide range of adhesion possible through control of the balance of some of the fatliquor components. Fatliquoring conditions were also very important. In the tannery the condition present at the time the fatliquor is deposited upon the leather fibers may well be of prime importance. Further work should consider the physical chemistry of the fatliquor emulsions as well as that of the leather itself.

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3. Cox, William R., and Roddy, W. T., *ibid.*
4. Association of Official Agricultural Chemists, Methods of Analysis.
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Studies in Chrome Tanning

XVIII. The Use of Naphthalenic Syntans as Adjuncts in Chrome Tanning

By Edwin R. Theis and W. R. Lotz

Stiasny in 1911 patented "a method for the synthetic manufacture of tanning substances". The products so manufactured by this process were

(From the Division of Leather Technology, Institute of Research, Lehigh University, Bethlehem, Pa. and the Technical Laboratories of the Albert Trostel and Sons Company, Milwaukee, Wis.)
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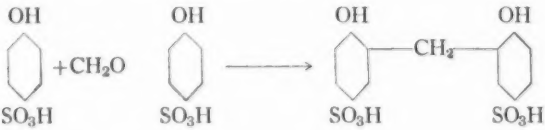
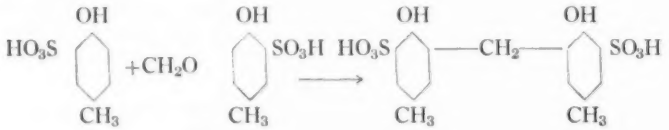
not in anyway related to the natural tanning agents. However, they react in a similar manner to these natural tannins in that they precipitate gelatin, protect hide substance treated with them from putrefaction and produce a leather like material of light color. During the past four decades, many modifications of the Stiasny process have been made and as a result, the tanning industry has at its disposal a very large choice of synthetic organic materials.

The Stiasny patent was immediately taken up by the German chemical industry and put on the market as "Neradol D". This so called first synthetic tanning material was made by the condensation of phenol sulfonic acid with formaldehyde, producing a mixture of substances—the simplest of which is dihydroxy-diphenylmethane-disulfonic acid:



or with cresol, the following equation represents the course of the theoretical chemical reaction:



However, in practice, the course of the reaction is somewhat different, due to the fact that commercial cresol is a mixture of the three different isomers and consequently a mixture of ten isomer dihydroxy-ditolylmethane-disulfonic acids can be expected. Schütte, investigating the formaldehyde condensation product of p-cresol-sulfonic acid, found that during the condensation process at least three of the following complexes are formed, (1) dihydroxy-ditolyl-monomethan-disulfonic acid, (2) trihydroxy-tritolyl-dimethan-disulfonic acid, (3) tetrahydroxy-tetratolyl-trimethan-disulfonic acid, and (4) pentahydroxy-pentatolyl-tetramethan-disulfonic acid.

With decreasing solubility, these high molecular complexes become more sensitive to salt and to strong acids and show less dispersing properties than the simpler condensation products with a comparatively large percentage of sulfonic acid groups. The less water soluble products are kept in a state of colloidal dispersion by the more water soluble ones.

In the course of a short time, many other organic sulfonated compounds were condensed with formaldehyde yielding products of more or less the same

tanning properties. Of all of these, the naphthalenic type were of the most commercial importance as adjuncts in the vegetable and chrome tanning process. The type "Neradol N" was made by sulfonating naphthalene and then condensing with formaldehyde.

The acid and neutral types of naphthalenic syntans have been used as auxiliary tanning agents both with vegetable extracts and with chrome liquors. Manufacturers of these products have advocated their use in the pickle (as a pretannage), in the chrome liquor itself, as a neutralizing or setting agent during the chrome tannage, as a "bleach" for making white chrome leather, and as a color leveler prior to coloring.

When naphthalenic syntans are added to regular chrome liquors, there are formed chromium complexes containing the anion of the syntan—if goodly amounts of these syntans or the chromium solution are too dilute, a grayish-white precipitate forms. The syntan-chromium complex is largely responsible for the whitish shade produced by treatment of chrome tanned leather "in the blue" with the naphthalenic syntan. These particular complexes are formed by replacement of "sulfato" groups by the anion of the syntan.

When the naphthalenic syntan is added to the pickle liquor, pretannage obtains since the shrinkage temperature of the treated skin increases. It is quite possible that the syntan tans through bridging of adjacent amino groups with the sulfonic acid groups of the syntan. An addition to the tannage obtaining, the syntan (at least the smaller complexes) penetrates more thoroughly into the skin during the pickling action and thus has a somewhat different action during the chrome tannage than would be the case if the syntan had been added directly to the chrome liquor.

Experimental

For the comprehensive studies planned, relative to the use of syntans as adjuncts, in chrome tanning, certain basic rules were used in setting up the experimental process:

1—Since the process was to be a combined drum bate, pickle-tan one, washing the limed stock became important. Experience indicated that 20 minutes were necessary and the temperature of the water used should raise the temperature of the stock slowly from out of lime temperature to that of bating.

2—The stock in most tanneries needs to be acid washed (remove lime blast). After the acid wash, a small amount of lime is added to rapidly raise the pH value to the optimum one for bating. Bating enzymes may be adversely affected by too low a pH value.

3—The bating was done with pancreatic enzymes—1 per cent. The temperature range was 80°-90°F. and the time not less than 40 minutes. Do not

worry about over-bating. The wash after bating was normal but should be sufficient for removing "scud" and solublized material.

4—The pickle use was a normal one, with salt and sulfuric acid. The time of drum pickling varies with the thickness of the stock and the "lime streak" desired.

5—In chrome tanning, it is preferable to use an aged sugar reduced chrome liquor. In the non-formate tannage, the result of using unmasked sulfur dioxide reduced liquor gave poor leather. In the formate stabilized tannage, sulfur dioxide and sugar reduced chrome liquors gave about the same results. For the tests outlined and discussed in this paper, sugar reduced chrome liquor was used, with a minimum time for penetration and tanning and a fairly long time of setting and neutralizing.

The tests discussed herein were made by the drum bate-pickle-and-tan procedure. For the manufacture of side leather, there are many variations of bating, pickling and chrome tanning; (a) paddle bating and paddle pickling and tanning, (b) paddle bating, paddle pickling and drum tanning, (c) paddle bating and drum pickling and tanning and (d) combined drum bating, pickling and tanning. This last procedure was chosen for the test series because the industrial trend is in that direction and further, the plants co-operating in these tests were very familiar with its advantages and disadvantages.

Both non-formate and formate chrome tannages are widely used with the formate type rapidly increasing in popularity especially for side leather manufacture. Some recent development by the allied industry has caused some shift from sodium formate to the calcium salt. Development along plant scale lines has indicated that little or no difference exists in what either of these salts will do and experience has shown that the trends indicated for sodium formate usage will obtain for calcium formate. Both formates were used in the tests given.

Information, by direct contact with many tanners, with representatives of the allied industry, and from stratigraphic analysis of many side leathers and their interpretation, have led us to believe that most non-formate chrome tanners neutralize and set their chrome tannage to about pH 2.9 to 3.2 and most formate-chrome tanners to about pH 3.7–4.2. For these reasons, we neutralized the non-formate chrome tannages to pH 3.1 and the formate chrome tannages to pH 4.0. In that way, we felt that we had taken average value presently used in the industry.

Setting up the average chrome tanning process, and especially the combined drum bate, pickle, and tan one, which had been chosen for these studies, became a real problem. Many factors had to be taken into account; (1) amount of washing out of the lime, (2) temperature of wash, (3) acid wash or no acid wash, (4) amount of bate, (5) type of bate, (6) time and

temperature of bate, (7) time of pickling, (8) type and amount of acid used in the pickle, (9) amount of salt used in the pickle, (10) at what point to use formate (with the pickle or with the chrome liquor, (11) basicity of chrome

TABLE I

THE COMBINED BATE-PICKLE-TAN PROCESSES USED

Non-Formato-Chrome Tannage		Formato-Chrome Tannage	
Stock—200 lbs. white weight*		Stock—200 lbs. white weight*	
Wash 20 minutes at 90°F.		Wash 20 minutes at 90° F.	
Drain		Drain	
Float 20 gals. water at 90° F.		Float 20 gals. water at 90° F.	
Acid Wash: 0.33% sulfuric acid 1 gal. cold water	5 min.	Acid Wash: 0.33% sulfuric acid 1 gal. cold water	5 min.
Add: 0.08% Hydrated Lime (in water suspension)	5 min.	Add: 0.08% Hydrated Lime (in water suspension)	5 min.
Bate: 1% Bate (pancreatic)	1 hour	Bate: 1% bate (pancreatic)	1 hour
Wash 15 minutes at 65-70° F.		Wash 15 minutes at 65-70°F.	
Drain		Drain	
Float 10 gals. water at 70°F.		Float 10 gals. water at 70°F.	
Pickle: 4½% salt	5 min.	Pickle: 4½% salt	5 min.
Add: 1¾% sulfuric acid 2 gals. cold water	60 min.	Add: 2% sodium formate (dry)	Start drum
		Add: 1¾% sulfuric acid 2 gals. cold water	60 min.
Tan**: 2¼ gals. 40% basic chrome liquor(with or without dissolved syntan or replacement tanning material)	2½ hours	Tan**: 2¼ gals. 40% basic chrome liquor (with or without dissolved syntan or replacement tanning material	2½ hours
Add: Bicarbonate of soda (and/or syntan) 3 gals. water at 90°F.	3 Feeds 30/30/40 min.	Add: Bicarbonate of soda (and/ or syntan) 3 gals. water at 90°F.	3 Feeds 30/30/30 min.
Add: Disinfectant	30 min.	Add: Disinfectant	30 min.
Pull and Pile***		Pull and Pile***	

*Stock: 200 lbs. white weight per test—out of 43-50 lb. hides of city butcher quality. Beam house process includes 1 day soak and 2 day unhairing.

**Chrome: 40% basicity sugar reduced liquor; 15% Cr_2O_3; aged for one week after reduction; syntans or other materials added just before using. RPM of drums =17.

***Color and Fat: Stock split in "blue" for 3 to 3½ oz. finished smooth dress leather; chrome retanned; 2% extract mordant; no syntan or replacement tanning material; alkaline fat-liquor.

liquor, (12) period of chrome tanning, (13) period of setting or neutralizing, (14) neutralizing agent, and (15) temperature at end of chrome tanning.

Each of these 15 points are controversial and certainly many of them are inter-related and are influenced by others, therefore, it was necessary to obtain a balanced process and the combined drum, bate, pickle and tan process adopted for both the non-formato- and the formato-chrome tannages are given in Table 1. The experimental processes used are not the production processes used by the cooperating tanneries since it would obviously be unfair to these tanneries to use a direct production formula on which they had spent time, money, and energy in perfecting and further more, to make these studies

more universal, it was necessary to use processes more nearly in accord with the large tanning industry. These process formulas are given in Table 1. Since the inception of this project, the processes outlined have been examined by other tanners and by the representatives of allied industry, without a real criticism.

The trends established for the various series of tests are not absolute because of differences in soaking, liming, bating, etc. in other tanneries. However, the trends established are important and provide a sound base from which to experiment and develop in other plants.

The analytical data herein given will be shown by stratigraph charts. These charts perhaps need a small amount of discussion. The stratigraphic (layer-wise) data have been obtained by splitting, 16 to 20 3-inch by 3-inch squares of leather (each square being taken from a side or skin) into at least 8 layers. The individual layers were then ground in a Wiley mill to a uniform powder for analysis. The splitting was accomplished by the use of a Model A, USMC, belt knife splitting machine. After grinding, each layer was analyzed for: moisture, hide substance, fat, insoluble ash, Cr_2O_3 water solubles, fixed organic materials (vegetable tannin, dyes, etc.), sulfato acidity, over-all basicity, and pH value. These data were then plotted on a chart as shown in the various stratigraphic charts. All of the data are given on a *moisture free basis*. Usually the layer-wise distribution is given for the leather in the "blue" immediately after wringing and in the "crust" just prior to finishing operations.

Thus the data given on the stratigraphic charts (layer-wise) show the protein (hide substance) density, the Cr_2O_3, fat, fixed organic matter, sulfato acidity, etc. distribution for each test. Changes in the layer-wise distribution for the tests made will be pointed out in detail as those tests are described and discussed.

1—Effect of Acid Naphthalenic Syntan Additions to Chrome Liquor Upon Chrome Tannage—*Series N*

The combined process of "bate-pickle and tan" has previously been described in detail both as to the non-formate and formate chrome tannage. Therefore for the Series N studies only the individual test will be described.

Eight to eleven sides were used for each test. The tests are as follows:

1—Control, using formate in the tannage but no syntan used in this test.

2—The same as (1) but adding 1.0 per cent acid naphthalenic syntan to the chrome liquor just prior to addition of the chrome liquor to the drum.

7—The same as (2) but in this case adding 3.0 per cent acid naphthalenic syntan to the chrome liquor.

3—The same as (2) but using *no formate* in the chrome tannage but adding the 1.0 per cent acid syntan to the chrome liquor as outlined in (2).

5—The same as (3) but using 3.0 per cent acid syntan with the chrome liquor.

8—The same as (3) but using 5.0 per cent acid syntan with the chrome liquor.

4—The same as (3) but using 0.6 per cent salt free acid naphthalenic syntan with the chrome liquor.

6—The same as (3) but using 1.8 per cent salt free acid syntan with the chrome liquor.

In all of the 8 tests, described above, the same degree of neutralization (standard amounts of sodium bicarbonate) during chrome tannage obtained. The final pH value of the chrome liquor (after neutralization) and the shrinkage temperature of the leather so produced are given in Table 2.

TABLE II

Test	After Bate	After Pickle	After Tan	After Neutralization	Shrinkage Temperature °C.
1	8.48	3.19	3.29	4.12	102°
2	8.42	3.18	3.20	3.98	100°
7	8.52	3.08	2.90	3.60	96°
3	8.42	1.20	1.90	3.30	86°
5	8.72	1.30	2.02	3.18	88°
8	8.55	1.19	2.78	2.87	81°
4	8.61	1.31	2.00	3.20	84°
6	8.72	1.20	1.85	3.10	83°

The leather after tanning was "mulled" for 24 hours, wrung, split and shaved. It was then processed to the finished state as described earlier in this report. The tanned leather was sampled after wringing (in the blue) and in the crust. A 4-inch x 4-inch piece was taken from each side—these samples were for stratigraphic chemical analysis. The data, so obtained, are shown in Figures 1-8.

These figures give stratigraphic data for the leather in the "blue" and in the "crust". The data for the leather in the "blue" are plotted on full scale (0-100 per cent thickness) while that for leather in the "crust" are plotted on one-half scale because the leather was split and shaved previous to the finishing operations. Such stratigraphic (layer-wise) plotting allows for ready comparison of the heavy leather in the "blue" and the less heavy leather in the "crust".

The data, taken immediately after the basic chrome tannage, indicate the effect of the acid naphthalenic syntan on the formate-chrome and non-formate (standard) chrome tannage. In other words, the acid syntan addition materially decreases both the equilibrium and final pH value of the tannage—resulting in a lowering of the shrinkage temperature of the leather at this

TABLE III

SMOOTH DRESS LEATHER—CRUST— *N SERIES*

Test	Firmness	Tear	Break	Grain	Layout	Fullness	Notes
1	Crust (Firm to Boney)	Good Fiber	Sl. Woody	Smooth	Fair	Good	
2	Crust (but softer than 1 and 3)	Good Fiber (like regular)	Good Tight	Smooth	Good	Good	
3	Hard	Fair to Good	So. Woody	Sl. Raise Some Smooth	Poor	Good	Slight grain crack probably because of firmness
4	Boney-Hard	Fair	So. Woody	Sl. Raise	Poor	Good	As above
5	Hard, Medium Mellow (Inconsistent)	Good (Long Fiber)	Tight	Some Pebbled Grain	Good	Good	
6	Hard to Soft (Inconsistent)	Good (Long Fiber)	Tight	Smooth	Good	Good to V.G.	
7	Sl. Firm	Papery	Sl. Woody	Sl. Prominent Sl. Cracky	Fair to Good	Good	Cracky
8	Sl. Firm to Mellow	Good	Good V. Tight	Smooth Cracky	Good	Good	Cracky
Production	Mellow Crispness	Long Fiber	Tight	Smooth	Good	Round V. Full	

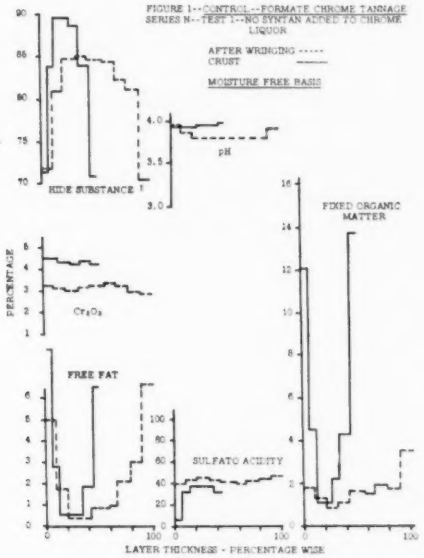


FIGURE 1--CONTROL--FORMATE CHROME TANNAGE
SERIES N--TEST 1--NO SYNTAN ADDED TO CHROME LIQUOR

AFTER WRINGING -----
CRUST ——

MOISTURE FREE BASIS

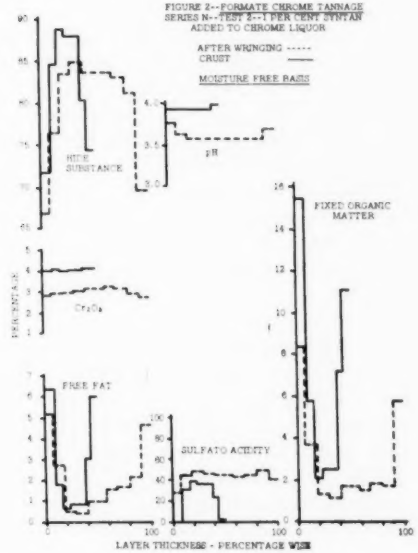


FIGURE 2--FORMATE CHROME TANNAGE
SERIES N--TEST 2--1 PER CENT SYNTAN ADDED TO CHROME LIQUOR

AFTER WRINGING -----
CRUST ——

MOISTURE FREE BASIS

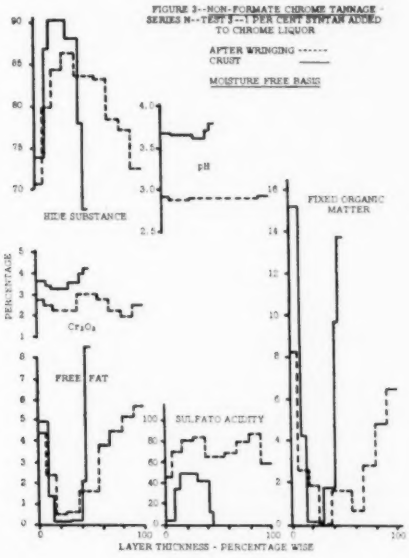
process stage. Since in this series (N Series) of tests, identical amounts of sodium bicarbonate were used for the neutralization, a wide range of final pH values obtain—this factor alone giving varying shrinkage temperatures.

The N-series data show some striking differences as the amount of acid naphthalenic syntan increases and a fair statement of fact is these studies represent a preliminary investigation of an exploratory nature, the data from which has certainly opened up many interesting and valuable avenues of thought. The data as presently presented graphically illustrate the results that might obtain if a tanner merely added some syntan to his chrome liquor without taking into account other adjustments (final pH value, neutralization, coloring, and especially the amount and type of fats used in the fat-liquoring process).

Figure 1 shows the stratigraphic data for the control test—a formate chrome tannage. These data indicate for moisture free basis, (1) the Cr_2O_3 fixed layer-wise is practically uniform for both the leather in the "blue" and in the "crust", (2) the sulfato acidity of the leather in the "blue" is for all intents and purposes uniform layer-wise but not for the leather in the "crust" state—due to the replacement of "sulfato" groups by the vegetable mordant and dye anions, (3) the fixed organic material in the "crust" state is about 12 per cent on the grain and 14 per cent on the flesh, and (4) the fat, in the grain, for the leather in the "blue" is 5 per cent while that for the leather in the "crust" is 8 per cent, indicating a large percentage of the fat in the finished state is due to the natural fat of the skin.

Figures 2 and 6 show data for 1 and 3 per cent syntan additions to the chrome liquor prior to its addition to the drum. Comparing Figure 2 with that of 1, it can be seen, (1) the Cr_2O_3 fixed on the grain and flesh (leather in the "blue") has been decreased while that in the center layers has remained unaffected—the slight chrome retannage in later processes corrects this factor (note "crust" data), (2) the sulfato acidity decreases on grain and flesh ("blue") due to the replacement of "sulfato" groups by the syntan anions—this factor for "crust" leather is further decreased by the vegetable mordant and dyes, (3) the fixed organic material for the leather in the "blue" is some 8.5 per cent on the grain and 6.0 per cent on the flesh—for the leather in the crust the grain value increases to 15.5 per cent while that for the flesh to some 11 per cent, and (4) the fat in the grain layer is apparently decreased by the acid syntan and the natural fat proportion relative to total fat in this layer is still larger than shown in Figure 1. A study of Figure 6 (3 per cent syntan added) indicates still further influence upon the Cr_2O_3 fixation, sulfato acidity, fixed organic material and on the redistribution of the natural fat.

A study of Figures 3, 4, and 5 show data relative to the use of 1, 3 and 5 per cent acid syntan in conjunction with non-formate chrome tannage. These tests show rather conclusively the effect of the acid syntan, when no formate is present to stabilize the tannage. These data show, that as syntan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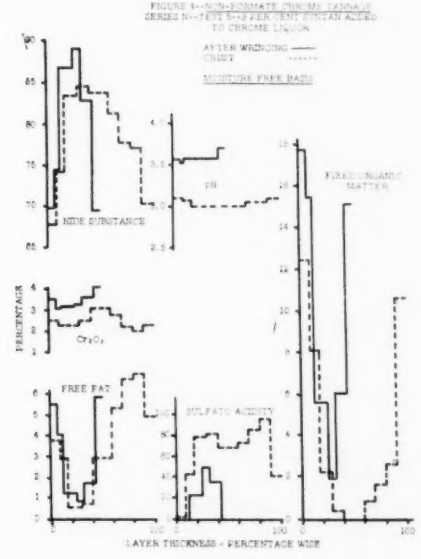
MOISTURE FREE BASIS
HIDE SUBSTANCE
pH
FIXED ORGANIC MATTER
PERCENTAGE
Cr_2O_3
FREE FAT
SULFATO ACIDITY
LAYER THICKNESS - PERCENTAGE WISE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PERCENTAGE
Cr_2O_3
FREE FAT
SULFATO ACIDITY
LAYER THICKNESS - PERCENTAGE WISE

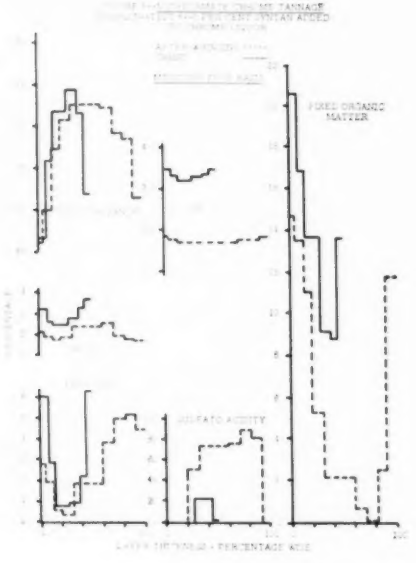
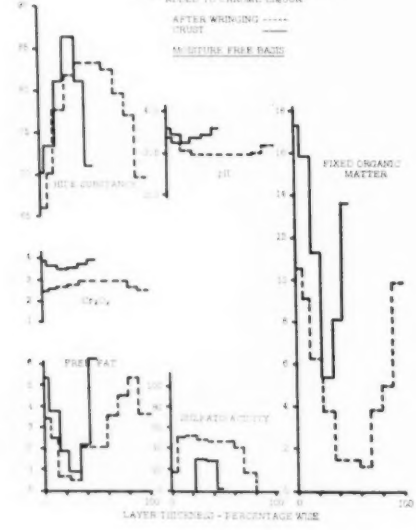


FIGURE 6.—FORMATE CHROME TANNAGE
SERIES N.—TEST 7·5 PER CENT SYNTAN ADDED TO CHROME LIQUOR



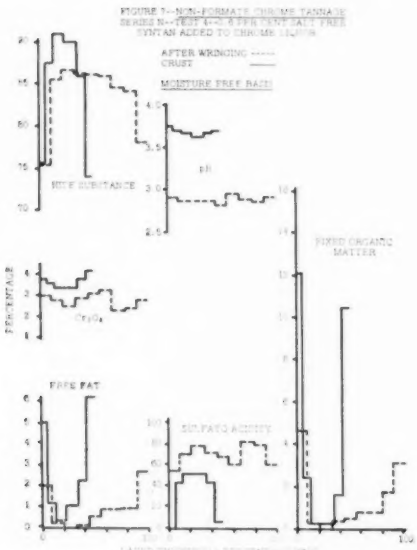
additions increase, (1) the Cr_2O_3 layer-wise fixation becomes very non-uniform, (2) the sulfato acidity increases greatly, (3) the fixed organic matter (leather in the "blue" increases on the grain layer from a very low amount to 8, to 13, to 15 per cent, while for the leather in the crust, this value increases from approximately 12 per cent (figure 1) to 15, to 18, and to 21 per cent.

Figures 7 and 8 show data for the use of a salt free acid syntan and indicate that similar results obtain as with the regular acid syntan used with non-formate chrome liquors.

The data given in Figures 1-8 may be summarized relative to both the leather in the "blue" and the leather in the "crust" as follows: (1) the formate introduced prior to the addition of the chrome liquor stabilizes the subsequent chrome tannage whether or not acid syntan is present, (2) the syntan or syntan plus mordant replaces sulfato groups in the chromium salt fixed, (3) when no syntan is present, the mordant fixed is some 12 per cent in the grain layer, whereas if acid syntan is present, the mordant fixed is 8 per cent or less—thus accounting to some extent for the change in color shade, (4) if formate is present, less drastic neutralization need obtain prior to coloring and fat-liquoring, (5) the chrome retannage (under the conditions obtaining for these tests) causes the Cr_2O_3 fixed during the retannage to be of the same trend as the basic chrome tannage but of a higher level, and (5) the syntan present appears to redistribute the natural fat present in the skins prior to the chrome tannage.

Table 3 gives the tannery sorting evaluation of the leather produced in this series of tests. These data may be summarized; (1) test 2 produced the best leather (figure 2), (b) the presence of formate during the chrome tannage causes the leather in the "crust" to be softer and more consistent in "temper", (c) increasing additions of acid naphthalenic syntan, above 1 per cent, to the non-formate chrome liquors causes the leather to become progressively "tighter" and "cracky"—the use of formate however eases the effect on the grain but not enough to offset the disadvantages relative to "crackiness", (d) some evidence is presented that salt free acid syntans may be advantageous, and (e) in all cases, the incorporation of formates with the tanning system, especially with syntan present, gave better leather than when formates were not present.

While the practical evaluation of the finished leather gave strong indication that the leather made by Test 2 was the best of the series, this evaluation does not preclude the possibility that by careful change of such factors as neutralization during tannage and change in fat liquor, results might be such as to show others of such tests to be as good as that given by Test 2. As mentioned earlier, the Series N tests were exploratory in nature and only one variable (syntan) was present. The Series N tests have led to many avenues of approach and the extension of these investigations will be discussed in detail as we proceed.


AFTER WRINGING
CRUST
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HIDE SUBSTANCE
pH
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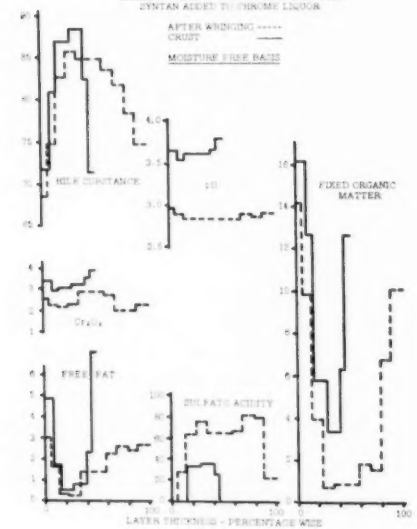
PERCENTAGE
ASH
FREE FAT
SULFATE ACIDITY
LAYER THICKNESS - PERCENTAGE WISE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FREE FAT
SULFATE ACIDITY
LAYER THICKNESS - PERCENTAGE WISE

2—Effect of Acid Naphthalenic Syntan Additions to Chrome Liquor upon Chrome Tannage—*Series Q*

In order to eliminate the variable final pH value during the chrome tannage—as discussed for Series N—another series of tests similar to the N Series were made. For this particular series, another acid naphthalenic syntan was used. In the Q-Series, the final pH values at the end of chrome tanning was adjusted to definite values. The modus operandi of this series was as follows:

TABLE IV

SHOWING VARIATION IN Q-SERIES TESTS

Test No.	Formate Added	Syntan* Added	Bicarbonate Added
1 (control)**	None	None	1.50 pounds
2	None	1% Acid	1.75 pounds
3	None	3% Acid	1.75 pounds
4 (control) ***	2%	None	1.75 pounds
5	2%	½% Acid	0.75 pounds
6	2%	1% Acid	1.16 pounds
7	2%	2% Acid	1.78 pounds
8****	2%	1% Neutral	0.75 pounds

*Acid Syntan—Tanak AA (American Cyanamid)
**Neutral Syntan—Tamol N (Rohm and Haas)
***Non-formato-chrome tannage control
****Formato-chrome tannage control

In all cases the acid syntan was added to the chrome liquor just prior to its addition to the drum. The data taken during the tannage are given in Table 5.

TABLE V

Test No.	After Bate	After Pickle	After Tan	After Neutralization	Shrinkage Temperature ° C.
1	8.68	1.52	2.30	3.28	94.0
2	8.62	1.40	2.00	3.10	94.0
3	8.72	1.51	1.91	2.93	92.5
4	8.77	3.49	3.37	4.09	107.0
5	8.72	3.96	3.70	4.00	104.5
6	8.68	3.76	3.58	4.04	102.5
7	8.66	3.62	3.30	3.97	99.5
8	8.58	3.78	3.65	3.97	103.0

It is self evident, from Table IV, that the Q-Series of 8 tests really represent two different tannages, the one, a standard chrome tannage, without the use of formates, but with varying additions of acid syntan, while the other represents a formato-chrome tannage with the same varying additions of acid syntan.

TABLE VI

SORTING EVALUATION

Q-Series Tests in Semi-finished State

(Albert Trostel and Sons)

Test	Firmness	Tear	Break	Grain	Fullness
1	Medium to Firm and Boney	Good	Tight	Smooth Very Slightly Cracky	Flat
2	Medium to Firm	Good to Dry	Tight	Smooth, Cracky	Flat
3	Soft to Firm Inconsistent	Some Dry Tear	Tight to Woody	Smooth, Cracky	Flat
4	Medium—Consistent	Good	Tight to Woody	Smooth	Good
5	Medium	Good	Tight	Smooth	Good
6	Medium–Soft	Good	Tight	Smooth	Good
7	Soft to Medium Inconsistent	Papery	Tight to Woody	Smooth, Cracky	Good
8	Medium to Firm Inconsistent	Good	Tight	Smooth, Very Slightly Cracky	Good

Samples of these 8 tests were taken in the "blue" and in the "crust" in the same manner as described for the N-Series. The stratigraphs are given in Figures 9-16.

The data given in Figures 9, 10, and 11 are for the non-formate chrome tannage with 0, 1, and 3 per cent acid syntan present. Figure 9 may be considered the non-formate chrome tannage control. The data shown by this figure indicate; (1) very erratic Cr_2O_3 distribution layer-wise, (2) a very high value of sulfato acidity for the leather in the "blue" and with some replacement of sulfato groups by the mordant and dye for the leather in the "crust" —especially in the grain and flesh layers, (3) a wide divergence of pH value of the leather in the "blue" as compared with the leather in the "crust", and (4) some 15 per cent fixed organic matter for the grain layer of the leather in the "crust".

The data given in Figures 10 and 11 are an interesting stratigraphic picture—(a) a decided decrease in Cr_2O_3 fixation in the grain and flesh layers, (b) a very high sulfato acidity with this factor drastically decreased in the grain and flesh layers—indicative of syntan replacement of sulfato groups for the leather in the "blue" and syntan and vegetable mordant anion replacement of sulfato groups for the leather in the "crust", and (c) a decreased

TABLE VII
SORTING EVALUATION
Q-Series Tests in Semi-finished State
(American Cyanamid Company)

Test No.	Cracky Grain	Feel	Break	Fullness	Firmness	Mellowness	Remarks (Syntan. Formate)
1	No Predominates	Generally Full	Good	Full to very full	Very	Some Tinniness Noted	None (Control)
2	No Predominates	Generally Good	About half good, half coarse, runny	Full to very full 50–50	Firm to over firm 50–50	None	No Formate 1% Acid
3	Yes Predominates	Generally Good	Coarse, runny, break predominates	Very	Very	Indication	No Formate 3% Acid
4	No	Good	More Good than Coarse and runny	Yes	Moderately Firm to Firm Mostly Firm	Yes	2% Formate No Syntan
5	No	Good	Same as No. 4	Yes	Yes	Yes. Some sides soft	2% Formate 1 ½% Acid
6	About 50–50	Full with tendency toward mellowness	Fair-Good. Coarse and runny predominates	Generally Full. Two sides empty and flat	Generally Firm. One side mushy.	Generally yes. Some sides tinny, some soft.	2% Formate 1% Acid
7	Yes Predominates	Good	From good to very coarse and runny. Mostly runny.	Yes	Yes	Somewhat mellow to mellow.	2% Formate 2% Acid
8	No Predominates	Generally good. Soft tendency.	Loose, runny, break in excess	From soft to very full—fairly even distribution.	From mushy to over firm Fairly even distribution.	Slightly mellow to soft.	2% Formate 1% Neutral

FIGURE 9--CONTROL--NON-FORMATE CHROME TANNAGE
SERIES Q--TEST 1--NO SYNTAN ADDED TO THE CHROME LIQUOR

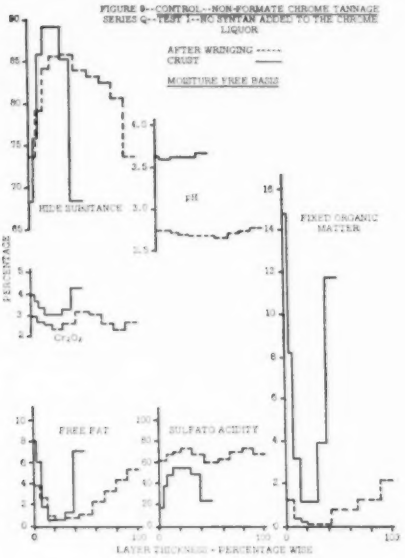
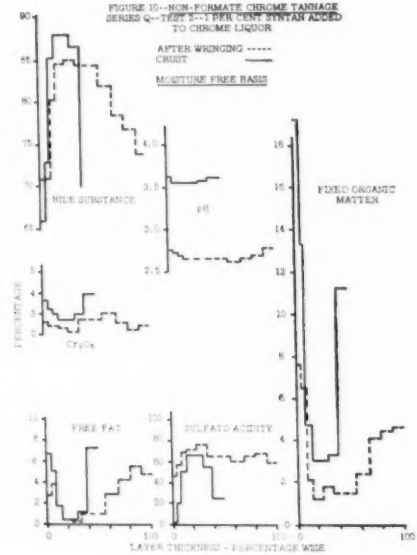


FIGURE 10--NON-FORMATE CHROME TANNAGE
SERIES Q--TEST 2--1 PER CENT SYNTAN ADDED TO CHROME LIQUOR



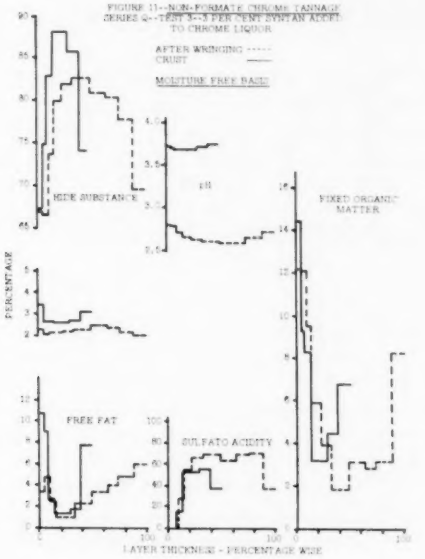


FIGURE 11.—NON-FORMATE CHROME TANNAGE
SERIES 2.—TEST 3.—3 PER CENT SYNTAN ADDED TO CHROME LIQUOR

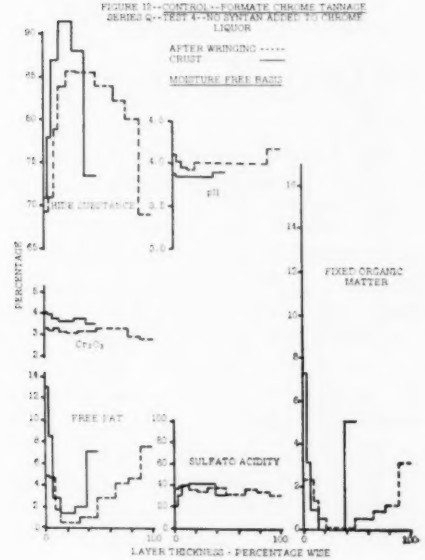


FIGURE 12.—CONTROL.—FORMATE CHROME TANNAGE
SERIES 2.—TEST 4.—NO SYNTAN ADDED TO CHROME LIQUOR

FIGURE 13--FORMATE CHROME TANNAGE
SERIES C--TEST 5--1.5 PER CENT SYNTAN
ADDED TO CHROME LIQUOR

AFTER WRINGING -----
CRUST ——

MOISTURE FREE BASIS

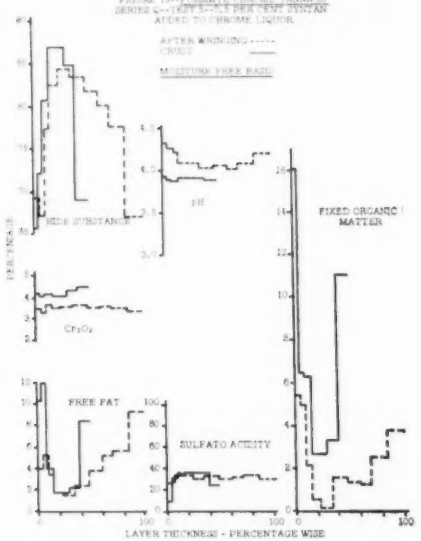
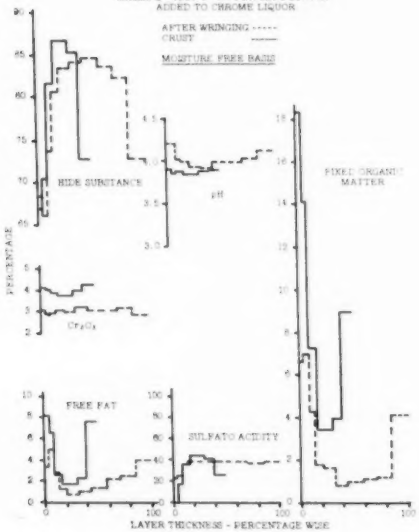


FIGURE 14--FORMATE CHROME TANNAGE
SERIES C--TEST 6--1.0 PER CENT SYNTAN
ADDED TO CHROME LIQUOR

AFTER WRINGING -----
CRUST ——

MOISTURE FREE BASIS



vegetable mordant and dye as syntan increases—thus bringing about a color shade difference.

Figures 12, 13, 14 and 15 show data for the formato-chrome tannage in the presence of 0, 0.5, 1, and 2 per cent acid syntan. Figure 12 may be considered the control tannage for the formato-chrome tannage system. These data show, (1) an almost level Cr_2O_3 fixation, (2) an almost level and low sulfato acidity for the leather in the "blue", (3) much lessened divergence of pH values between the leather in the "blue" and the "crust" and with the pH value of the leather in the "crust" having a lower pH value than that of the leather in the "blue", and (4) only some 7 per cent vegetable mordant and dye fixed.

Figures 13, 14, and 15 show the effect of the syntan additions to the system—not nearly as drastic as that obtaining for the non-formate chrome tannages systems. It will be noticed that even with 2 per cent syntan addition, the Cr_2O_3 fixed is only slightly decreased on the grain layer and the same holds for the sulfato acidity of the finished leather. It should be noted that even with the larger amounts of syntan present, the syntan fixation is largely on the grain and flesh layers and that it does not penetrate entirely through the skin. The different amounts of vegetable mordant and dye fixed may account for the color shade differences noted from test to test.

Figure 16 shows data for the addition of a neutral syntan to the chrome liquor. The data shown in this figure will be discussed later in the R-Series.

Summarizing the stratigraphic data given in the Figures 9-16, it can be stated; (1) the presence of formate stabilizes even the syntan chrome liquors, as this syntan appears to redistribute the natural fat present in the skin at the time of tannage, and (2) the presence of small amounts of acid syntan bring about improvement in the formate-chrome tanned leather.

The 8 Series-Q test leathers were independently sorted by the tannery and the supplier of the acid syntan. These leathers were examined in the "crust" and in the finished condition. Tables 6, 7, 8 show the usual sorting evaluation. A final sorting evaluation was made on the finished leather, using the method of weight evaluation described by C. D. Wilson. This evaluation was made "side-wise" so that all characteristics of each and every side could be noted—that is, each side was examined for "tightness", "feel", "crackiness", and "fullness". Table 9 gives the careful "side-wise" evaluation. Comparison of data given in Tables 6, 7, 8 are of interest since they represent two distinct sortings and in the main the comparisons are good. These data should then be compared with the "side-wise" evaluation. The data given in Table 8 was then recalculated to give that in Table 9.

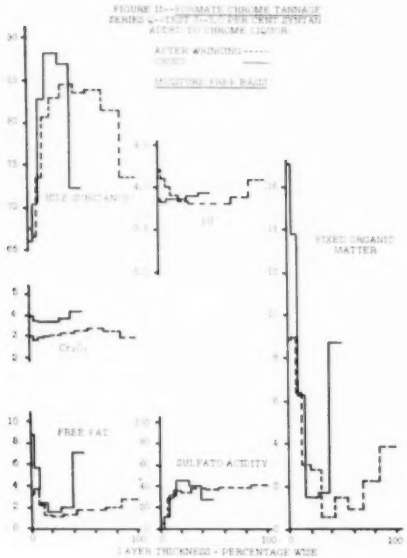


FIGURE 16--FORMATE CHROME TANNAGE
SERIES C---TEST B---1% PER CENT NEUTRAL CYNTAN ADDED TO CHROME LIQUOR

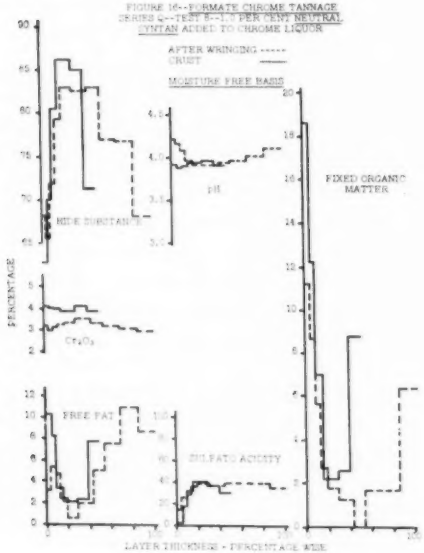


TABLE VIII

SORTING EVALUATION AS MADE AT THE TANNERY

Series Q (finished leather)

Test No.	Total No. of Skins	CHARACTER			FEEL				CRACKINESS			FULLNESS		
		Tight	Fairly Tight	Loose	Soft	Mellow	Medium	Firm	None	Tendency	Crack	Full	Medium	Flat
P*	9	2	7	0	1	4	2	2	9	0	0	5	2	2
1	9	8	1	0	0	0	1	8	7	2	0	2	3	4
2	9	5	4	0	0	1	2	6	3	6	0	5	4	0
3	9	4	4	1	1	1	1	6	3	1	5	8	1	0
4	9	4	5	0	0	3	4	2	8	1	0	8	1	0
5	9	6	2	1	0	4	2	3	8	1	0	6	2	1
6	9	8	1	0	0	2	2	5	2	5	2	7	1	1
7	9	5	3	1	1	1	5	2	4	3	2	7	1	1
8	9	5	4	0	2	3	1	3	3	4	2	9	0	0

*Denotes production sides.

GRADING

Test No.	Pieces	Grade 1	Grade 2	Grade 3	Grade 4	Grade 5
P	9	0	4	4	1	0
(1)	9	0	1	1	3	4
(2)	9	0	0	5	2	2
(3)	9	0	0	2	4	3
(4)	9	0	1	5	3	0
(5)	9	0	1	2	5	1
(6)	9	0	1	3	4	1
(7)	9	0	1	3	5	0
(8)	9	0	3	0	5	1
Totals	81	0	12	25	32	12

TABLE IX

SHOWING INDEX SORTING EVALUATION

Test No.	Character	Feel	Crackiness	Fullness	Grade	Over-all Quality
P*	2.22	2.22	3.00	2.33	3.33	90.82
1	2.88	1.11	2.77	1.77	1.89	76.56
2	2.55	1.44	2.33	2.55	2.33	73.84
3	2.33	1.44	1.77	2.89	1.89	67.37
4	2.44	2.11	2.89	2.89	2.77	83.76
5	2.55	2.11	2.89	2.55	2.33	84.10
6	2.89	1.66	2.00	2.66	2.44	77.82
7	2.44	1.88	2.22	2.66	2.55	75.50
8	1.88	2.00	2.11	3.00	2.55	69.27

*Regular Production Sorting Evaluation

The calculated or sorting index data were obtained as follows:

STATISTICAL EVALUATION CALCULATION

CHARACTER Weight + value given	Tight 3	Fairly Tight 2	Loose 1
Example—Test 1			
No. of skins in each category	8	1	0

$$\text{Calculation factor} = \frac{3 \times 8 + 2 \times 1 + 1 \times 0}{9} = 2.88 \quad \text{(best value = 3.00)}$$

FEEL Weight Value given	Soft 2	Mellow 3	Medium 2	Firm 1
Example—Test 1				
No. of skins in each category	0	0	1	8

$$\text{Calculation factor} = \frac{2 \times 0 + 3 \times 0 + 2 \times 1 + 1 \times 8}{9} = 1.11 \quad \text{(best value = 3.00)}$$

CRACKINESS Weight value given	None 3	Tendency 2	Cracky 1
Example—Test 1			
No. of skins in each category	7	2	0

$$\text{Calculation Factor} = \frac{3 \times 7 + 2 \times 2 + 1 \times 0}{9} = 2.33 \quad \text{(best value = 3.00)}$$

FULLNESS Weight value given	Full 3	Medium 2	Flat 1
Example—Test 1			
No. of skins in each category	2	3	4

$$\text{Calculation factor} = \frac{3 \times 2 + 2 \times 3 + 1 \times 4}{9} = 1.77 \quad \text{(best value = 3.00)}$$

GRADE SORT Weight value given	1st 5	2nd 4	3rd 3	4th 2	5th 1
Example—Test 1					
No. of skins in each category	0	1	1	3	4

$$\text{Calculation factor} = \frac{5 \times 0 + 4 \times 1 + 3 \times 1 + 2 \times 3 + 1 \times 4}{9} = 1.89 \quad \text{(best value = 5)}$$

For over-all sorting evaluation, a further calculation can be made. Assuming

Character to be 40 per cent of the whole evaluation
Feel to be 25 per cent of the whole evaluation
Crackiness to be 25 per cent of the whole evaluation
Fullness to be 10 per cent of the whole evaluation

Then for Test 1, using data from table:

Character	$40 \times \frac{2.88}{3.00} =$	38.30
Feel	$25 \times \frac{1.11}{3.00} =$	9.26
Crackiness	$25 \times \frac{2.77}{3.00} =$	23.10
Fullness	$10 \times \frac{1.77}{3.00} =$	5.89
	Total=	76.55

therefore, the over-all sorting evaluation for Test 1 is 76.55 per cent.

The data shown in Table 9 was then plotted and is given in Figure 17. A careful study of this particular chart yields valuable information and trends: (1) the effect of formate additions during chrome tannage is again proven of real advantage, (2) for non-formate chrome tannage, syntan additions to the chrome liquor promote better "feel", more "fullness", a decrease in "tightness" (character), and greater tendency to crack, and (3) for formato-chrome tannage, syntan additions tend to give increased "tightness" (character), no real effect on "feel" and "fullness", and up to 0.5 per cent syntan addition no "crackiness"—with greater concentrations of syntan, however, "crackiness" obtains.

It is to be noticed that the 8 Q-Series tests are compared with regular production leathers of the same type. The over-all sorting evaluation or "quality percentage" shows rather strikingly, (1) the effect of formate in the chrome tannage, (2) the effect of syntan additions to the non-formate chrome tannage, and (3) the effect of syntan additions to formato-chrome tannage. The "quality percentage" data agrees well with the data presented in Table 8.

The data given for the Q-Series of tests substantiates the data taken in the N-Series, namely, that small amounts of an acid naphthalenic syntan, added to the chrome liquor just prior to its addition to the drum exert a real beneficial effect on the finished leather relative to "tightness", "feel", and "fullness" without bringing about any real degree of grain "crackiness".

3—Effect of Neutral Naphthalenic Syntan Additions to Chrome Liquor Upon Chrome Tannage—*Series R*

Parts 1 and 2 discussed the effect of the acid naphthalenic syntans when added to the chrome liquor and this liquor in turn used for the chrome tannage. For certain purposes, the neutral type of naphthalenic syntan has been

FIGURE 17--SORTING EVALUATION INDEX
SERIES Q--TEST 1-8

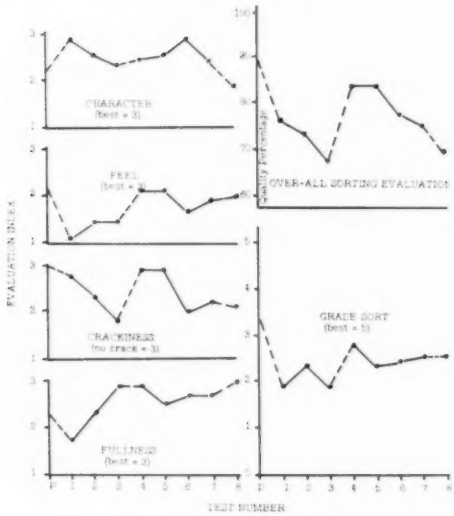
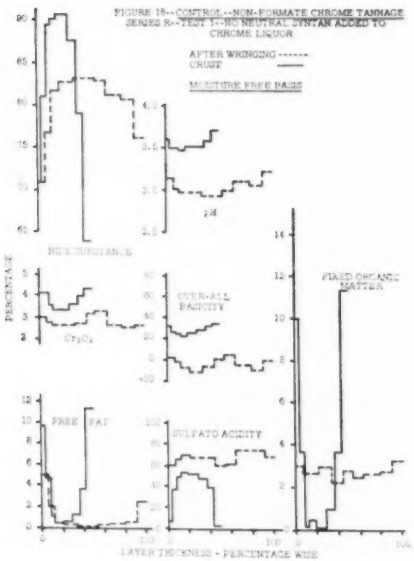


FIGURE 18--CONTROL--NON-FORMATE CHROME TANNAGE
SERIES R--TEST 1--NO NEUTRAL SYNTAN ADDED TO CHROME LIQUOR



advocated. For this reason, a series of 12 tests was made using the neutral syntan as an adjunct in chrome tanning.

The syntan was used in conjunction with a 40 per cent basic sugar reduced chrome liquor. In all 12 tests 200 pounds of white weight medium stock was used. The tests made were as follows:-

TABLE X

Test No.	Formate	Syntan*	Neutralization
Control (1)	None	None	1 ⅓lbs. Bicarb.
2	None	1% Neutral	1 lb. - ⅓oz. Bicarb.
3	None	3% Neutral	1 1/6 lbs. Bicarb.
4	2%	None	1 lb. -13 oz. Bicarb.
5	2%	1% Neutral	1-¼ lbs. Bicarb.
6	2%	3% Neutral	1-¼ lbs. Bicarb.
7	2%	None	¼% Neutral Syntan
8	2%	None	1% Neutral Syntan
9	2%	None	(1% Neutral Syntan (1-¼ lbs. Bicarb.
10	None	None	(1% Neutral Syntan (1 lb. -10 oz. Bicarb.
11	None	1% Neutral (Pretan)	1-¼ lb. Bicarb.
12	2%	1% Neutral (Pretan)	1-¾ lb. Bicarb.

*Neutral Syntan—Tamol N

Note: Tamol N used as pretan was dissolved in 2 gals. of water and added 2 minutes after the pickle acid.

TABLE XI

BATE-PICKLE-AND-TANNAGE DATA

Test No.	pH	After Bate	After Pickle	After Tan	After Neut.	Shrink Temp. ° C.
1		8.69	1.52	2.22	3.13	88.0
2		8.62	1.55	2.31	3.09	89.5
3		8.62	1.49	2.30	3.11	82.5
4		8.70	3.39	3.22	3.92	101.0
5		8.60	3.57	3.29	3.82	106.2
6		8.57	3.50	3.40	3.90	102.0
7		8.52	3.37	3.12	3.09	94.5
8		8.70	3.58	3.42	3.38	97.0
9		8.62	3.47	3.27	3.91	104.0
10		8.52	1.31	1.90	3.00	91.5
11		8.64	1.60	2.29	3.20	89.0
12		8.61	3.35	3.11	3.80	102.0

TABLE XII

SORTING EVALUATION INDEX

SERIES R—Smooth Dress Leather—Evaluation at Finish Sort

	CHARACTER BREAK				GRAIN			
Test No.	Good Tight	Fair	Poor Loose	Index	Smooth	Med.	Drawn	Index
1	7	4	0	2.64	11	0	0	3.00
2	9	3	0	2.75	11	0	0	3.00
3	8	3	0	2.73	9	2	0	2.82
4	5	5	0	2.50	9	1	0	2.90
5	7	2	1	2.60	10	0	0	3.00
6	8	2	0	2.80	9	1	0	2.90
7	2	7	0	2.22	9	0	0	3.00
8	3	4	3	2.00	10	0	0	3.00
9	5	3	0	2.63	8	0	0	3.00
10	1	7	2	1.90	8	2	0	2.80
11	5	6	0	2.46	9	2	0	2.82
12	8	1	0	2.89	9	0	0	3.00

	TEMPER				
Test No.	Soft	Optimum	Med.	Boney	Index
1	0	1	4	6	1.55
2	1	4	4	2	2.18
3	0	6	3	2	2.36
4	0	2	3	5	1.70
5	2	5	3	0	2.50
6	0	6	4	0	2.60
7	0	2	6	1	2.11
8	0	1	4	5	1.60
9	0	5	1	2	2.37
10	0	1	3	6	1.50
11	0	1	3	7	1.46
12	0	5	1	3	2.22

	CRACKINESS				FULLNESS			
Test No.	None	Tendency	Crack	Index	Full	Med.	Flat	Index
1	4	4	3	2.09	5	6	0	2.46
2	2	4	5	1.73	8	3	0	2.73
3	0	5	6	1.45	6	4	1	2.46
4	7	3	0	2.70	5	2	3	2.20
5	7	3	0	2.70	7	3	0	2.70
6	6	3	1	2.50	9	1	0	2.90
7	7	2	0	2.78	4	4	1	2.33
8	8	2	0	2.80	5	2	3	2.20
9	7	1	0	2.87	7	0	1	2.75
10	4	3	3	2.10	4	4	2	2.20
11	5	4	2	2.27	8	2	1	2.64
12	4	4	1	2.33	7	1	1	2.67

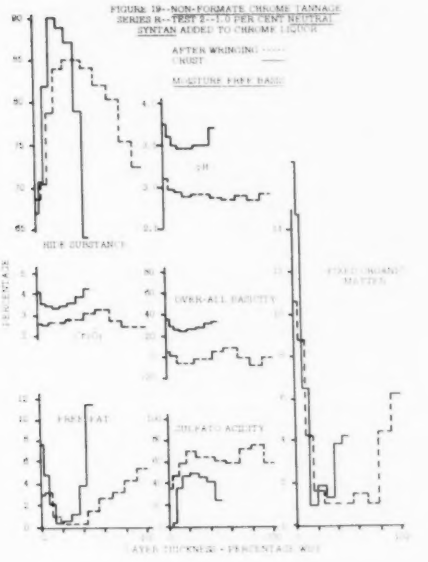
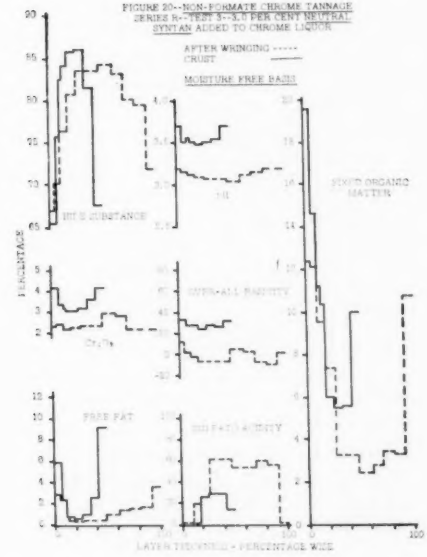


FIGURE 20.--NON-FORMATE CHROME TANNAGE
SERIES R--TEST 3--3.5 PER CENT NEUTRAL SYNTAN ADDED TO CHROME LIQUOR



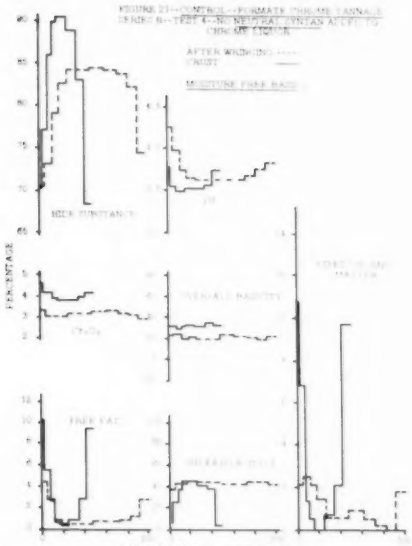
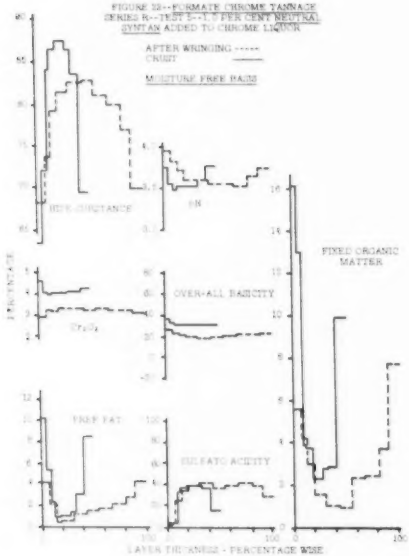


FIGURE 32--FORMATE CHROME TANNAGE
SERIES B--TEST 5--1.5 PER CENT NEUTRAL SYNTAN ADDED TO CHROME LIQUOR



The tables and charts show the data obtained from the stratigraphical chemical analyses of the leather and the sorting evaluation of the finished smooth side leather.

Tests 1, 2, and 3 (Figures 18, 19, and 20) show the effect of additions of neutral syntan to a non-formate chrome tannage. These data indicate the same general effects as were produced through the additions of acid syntan to chrome liquors—effect on Cr_2O_3 distribution, effect on sulfato acidity and effect on fixed organic matter. Further, the sorting evaluation index is approximately the same relative to character (tightness), and grain smoothness, a decided decrease in the index relative to crackiness as the amount of syntan is increased, an increase in temper as the syntan increases, and a maximum fullness with the use of 1.0 per cent syntan.

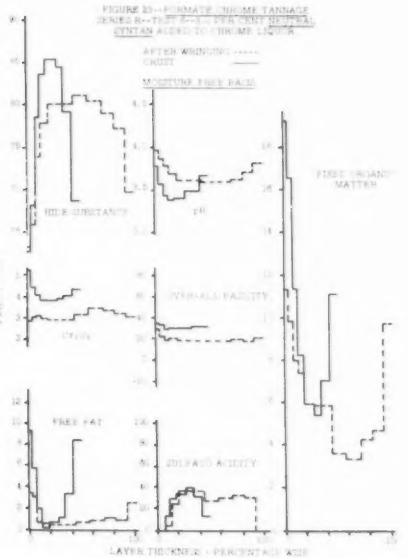
Tests 4, 5, and 6 (Figures 21, 22, and 23) give similar data to Tests 1, 2, and 3 but in Tests 4, 5, and 6, the syntan was acting in conjunction with the formato chrome liquor. Again we see the beneficial effects of formate and the combined beneficial effects of formate and syntan—as was demonstrated previously for the use of acid syntans.

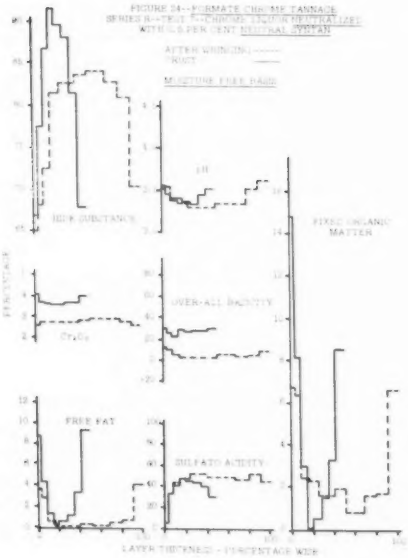
The factory sorting evaluation indicated Test 5 (Figure 22) to be the best leather with Test 6 (Figure 23) following a close second. The sorting evaluation index shows Test 5 and Test 6 to be of the same order but "crackiness" being the deciding factor since in certain other characteristics (such as tightness, temper, and fullness) leather from Test 6 would be judged the best leather.

The stratigraphs of leather from Tests 4, 5, and 6 show similar trends to those tests using the acid syntan and formate, controlled Cr_2O_3 distribution, decreased fat (both natural and that from the fat liquor in the grain layer as the amount of syntan increases), decrease in pH value in the finished leather as compared to the same leather in the blue but an increase in real basicity regardless of the pH drop, decreased sulfato acidity, and an increase in fixed organic matter with increased syntan additions.

Tests 7, 8, 9, and 10 (Figures 24, 25, 26, and 27) give data relative to the use of neutral naphthalenic syntans as neutralizing agents in the formato and non -formato chrome tannages. Again, we see the real value of the formate in the chrome tanning operation (compare Test 9 with 10). The sorting evaluation index indicates Test 9 to be the best of this series but not equal to Test 5 or 6.

The stratigraphs of leathers from Tests 7, 8, 9 and 10 show again the influence of formate-chrome tannage and also show the effect of the neutral syntan neutralization—with this type of syntan additions, the effect on the Cr_2O_3 in the grain and flesh layers appears to be more noticeable, especially when formate is present. Neutralization with a mixture of neutral syntan and sodium bicarbonate appears to give a better neutralization as can be seen from the pH values, the real basicity and sulfato acidity figures. The basicity data given in the R-Series of tests was made by the Lehigh Method of de-


AFTER WRINGING
CRUST
MOISTURE FREE BASIS
HIDE SUBSTANCE
pH
FIXED ORGANIC MATTER
Cr2O3
OVER-ALL BASICITY
FREE FAT
SULFATE ACIDITY
LAYER THICKNESS - PERCENTAGE WISE


AFTER WRINGING
CRUST
MOISTURE FREE BASIS
HIDE SUBSTANCE
pH
FIXED ORGANIC MATTER
Cr2O3
OVER-ALL BASICITY
FREE FAT
SULFATE ACIDITY
LAYER THICKNESS - PERCENTAGE WISE

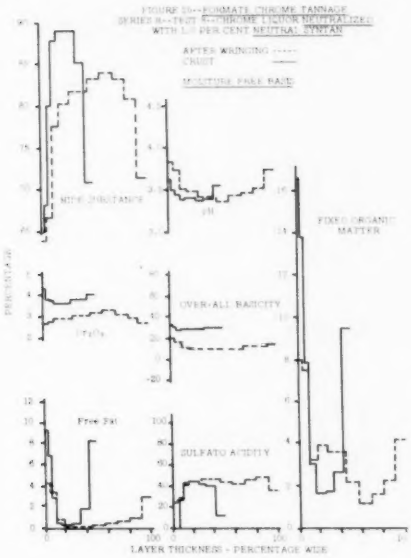
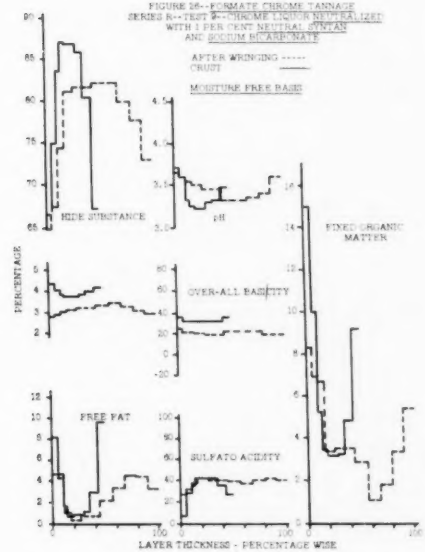


FIGURE 26--FORMATE CHROME TANNAGE
SERIES R--TEST 9--CHROME LIQUOR NEUTRALIZED WITH 1 PER CENT NEUTRAL SYNTAN AND SODIUM BICARBONATE



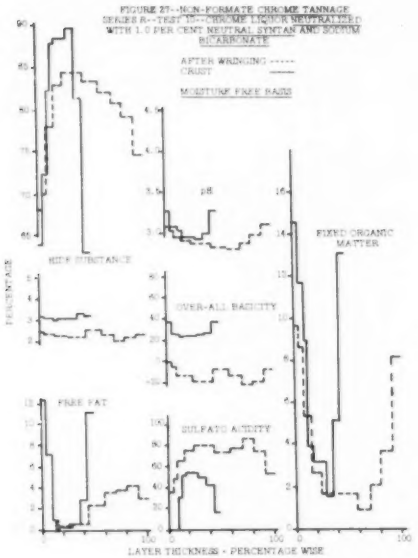


FIGURE 27.--NON-FORMATE CHROME TANNAGE. SERIES B.--TEST 15.--100,000 LIQUOR NEUTRALIZED WITH 1.5 PER CENT NEUTRAL SYNTAN AND 500/00 BICARBONATE.

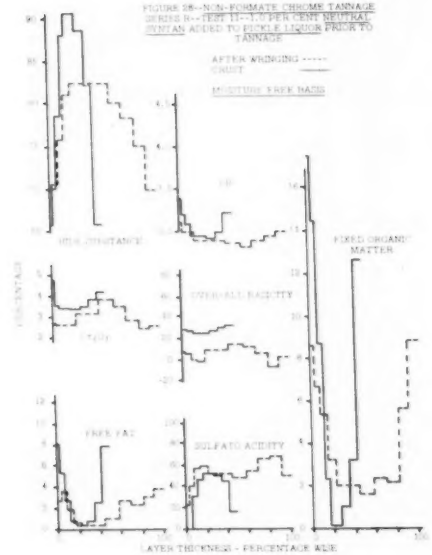
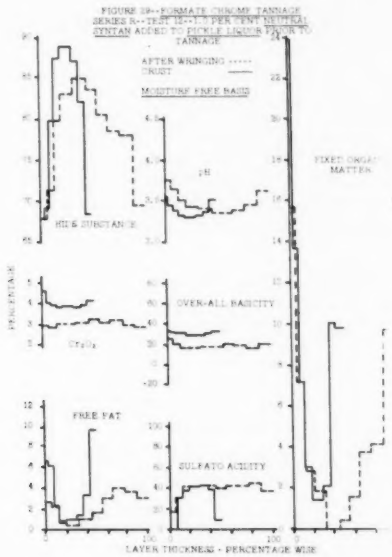
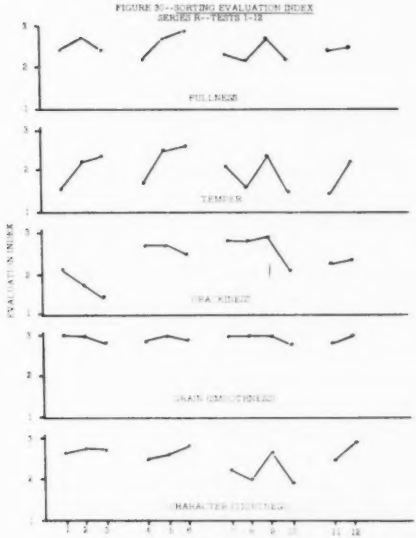


FIGURE 28.--NON-FORMATE CHROME TANNAGE. SERIES B.--TEST 11.--1.0 PER CENT NEUTRAL SYNTAN ADDED TO PICKLE LIQUOR PRIOR TO TANNAGE.


AFTER WRINGING
CRUST
MOISTURE FREE BASIS
HIDE SUBSTANCE
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
SULFATE ACIDITY
LAYER THICKNESS - PERCENTAGE WISE


FULLNESS
TEMPER
GRAIN (SMOOTHNESS)
CHARACTER (FIRMNESS)
EVALUATION INDEX
TEST NUMBER

termining leather over-all basicity and is described elsewhere. This over-all basicity of leather has the same meaning as that for the basicity of a chrome liquor. The present authors believe this factor to be as important as pH value and other factors for quality control.

Tests 11 and 12 (Figures 28 and 29) give data relative to pretannage with neutral syntan (added to pickle) and then chrome tannage both with and without formate additions. A comparison of data given in Test 11 (non-formato) and in Test 12 (formato) shows again the drastic influence of formate —this is especially noted for the Cr_2O_3 distribution, pH, basicity, and sorting index.

Of the 12 tests of this Series (R), Test 5 was given the highest rating with Test 6 being a close second—this was shown not only by the sorting evaluation index data but by the over-all sort made by the tannery. These data are shown graphically in Figure 30.

4—Effect of Acid Syntan Additions To Chrome Liquor Upon Chrome Tannage—*Series QR*

The Series Q tests were made in the pilot plant of the Albert Trostel and Sons Company and were of such interest that this series was repeated in the plants of the Fred Rueping Leather Company and the Prime Tanning Company. The repeat studies were very necessary since very often different beam house procedures play a very important role in the end result. In the case of the Fred Rueping Leather Company, advantage was taken of their formate-chrome tanning procedure which differs from that of the Trostel organization. The investigations made at the Prime Tanning Company were such as to use stock split "out of lime" whereas the stock at Trostel and Rueping was split in the "blue". In all cases, however, the combined operations of "bate-pickle and tan" were as presently utilized in those plants and while the actual procedure differed, the principle did not.

The QR Series were as follows: test 1, 200 pounds white weight stock made by the regular production formula to be used as control, test 2, identical with test 1 with the exception that the neutralization during chrome tannage was carried to pH 4.4 in place of 4.1, test 3, identical with test 2 but in this case 0.5 per cent acid naphthalenic syntan was added to the chrome liquor, test 4, identical with test 2 but 1.0 per cent acid syntan was added to the chrome liquor, and test 5, identical with test 2 but 1.5 per cent acid syntan was used. The acid syntan used was Tanak AA and calcium formate was used in all 5 tests.

As was the case for the other series of tests, the individual tests were sampled in the "blue" and "crust" states. The "blue" samples for this series however, were taken after splitting and shaving. The leather in the finished

condition was carefully sort evaluated. The data taken are shown in Figures 31, 32, 33, 34, 35, 36, and 37 and in Tables XIII, XIV, and XV.

TABLE XIII

PHYSICAL TEST DATA

Showing Mean Value and Probable Error

	Tensile (psi) N = 10		Grain Crack (lb. / in.) N = 20		Stitch Tear (lb./in.) N = 10		% Stretch at 50 lb. N = 10	
Test No.	Mean/PEM		Mean/PEM		Mean/PEM		Mean/PEM	
1	2350	199	4752	284	909	81	41.15	3.19
2	2551	149	6260	409	1019	102	38.15	2.31
3	2777	186	5805	269	1112	75	33.40	1.95
4	2840	188	6128	349	1095	95	33.90	1.70
5	2740	212	6079	423	1135	102	33.76	2.32

TABLE XIV

Showing Number of Skins in Each Category and the Sorting Evaluation Index

	Break				Grain			
Test No.	1	2	3	Index	1	2	3	Index
1	1	5	4	2.3	0	4	6	2.6
2	3	4	3	2.0	1	5	4	2.3
3	1	6	3	2.2	1	6	3	2.2
4	2	3	5	2.3	3	4	3	2.0
5	7	3	0	1.3	8	0	2	1.4

	Fullness				Temper				
Test No.	1	2	3	Index	1	2	3	2	Index
1	6	4	0	1.4	0	1	7	2	2.7
2	4	5	1	1.7	1	0	6	3	2.5
3	1	3	6	2.5	1	3	6	0	2.5
4	3	5	2	1.9	4	3	2	1	1.8
5	3	3	4	2.1	1	6	2	1	2.1

The data given in Figures 31-37 are of real interest since these data are a check on Series Q, made in a different tannery, and although a formate chrome tannage was used, there was a distinct variation in the bating, pickling, and formate-chrome tannage.

Within the Series 2-3-4-5 (Figures 31, 33, 34, 35, 36 and 37) the only variables are the amount of syntan and the amount of borax used to give a constant pH. Under these conditions: (1) large amounts of acid syntan produce poor break; (2) 1 per cent and 1-½ per cent acid syntan affect the temper significantly; (3) in general, acid syntan produces rough grain; (4) in general, 1 and 1.5 per cent acid syntan reduces fullness; (5) in general, syntan produces: (a) stretchier leather, (b) increased tensile strength, (c) slightly decreased grain strength, (d) increased stitch tear strength.

Within the Series 1-2 (Figures 31, 32, 33, and 37) the only variable is the final pH of neutralization and thus: (1) increased neutralization produces looser break; (2) increased neutralization affects temper only slightly; (3) in-

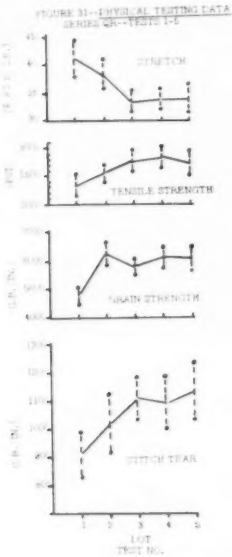
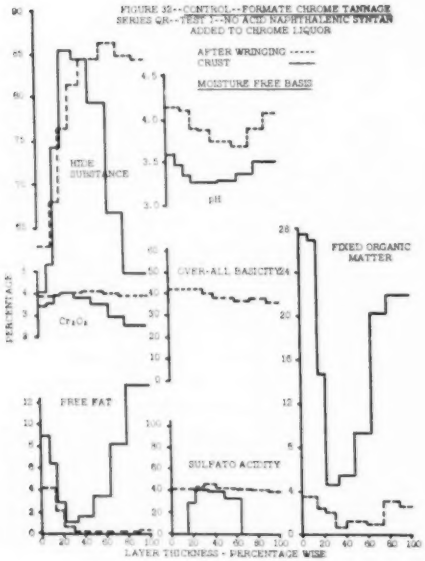


FIGURE 32--CONTROL--FORMATE CHROME TANNAGE
SERIES QR--TEST 3--NO ACID NAPHTHALENIC SYNTAN ADDED TO CHROME LIQUOR



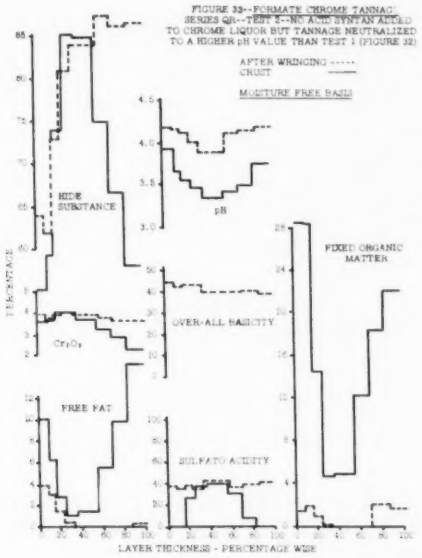


FIGURE 33--FORMATE CHROME TANNAGE SERIES QR--TEST 2--NO ACID SYNTAN ADDED TO CHROME LIQUOR BUT TANNAGE NEUTRALIZED TO A HIGHER pH VALUE THAN TEST 1 (FIGURE 32)

AFTER WRINGING -----
CRUST ——

MOISTURE FREE BASIS

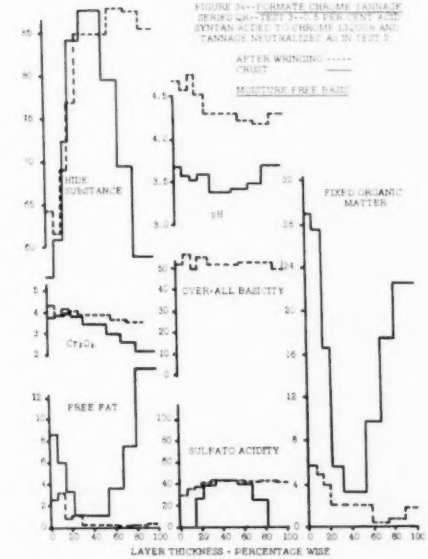
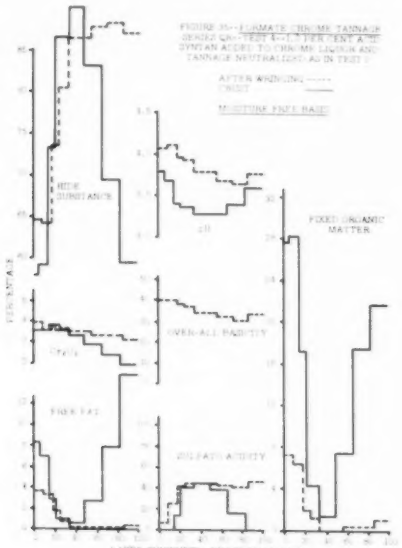
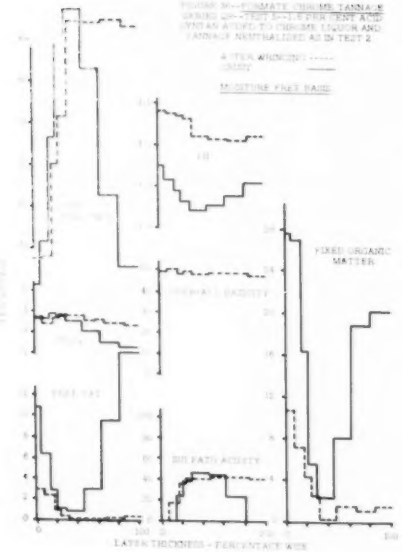


FIGURE 34--FORMATE CHROME TANNAGE SERIES QR--TEST 3--AFTER TEST 2 THE SYNTAN ADDED TO CHROME LIQUOR AND TANNAGE NEUTRALIZED AS IN TEST 3

AFTER WRINGING -----
CRUST ——

MOISTURE FREE BASIS


HIDE SUBSTANCE
FIXED ORGANIC MATTER
OVER-ALL BASICITY
FREE FAT
SO3 FATO ACIDITY
LAYER THICKNESS - PERCENTAGE AGE


FIXED ORGANIC MATTER
FREE FAT
SO3 FATO ACIDITY
LAYER THICKNESS - PERCENTAGE AGE

creased neutralization produces rougher grain; (4) increased neutralization produces increased fullness; (5) increased neutralization produces: (a) increased stitch tear strrength, (b) increased grain strength, (c) increased tensile strength, (d) less stretch.

It is of interest to study the stratigraphs of the 5 different tests of the QR Series. The over-all basicity data of this series are decidedly higher (in the blue) than those data of Series Q. The Cr_2O_3 fixation was lowered by the addition of the syntan as has been the case for all the syntan series. The sulfato acidity has been altered in the same manner as has obtained in all the syntan series studies to date.

The decrease in pH value of the leather in the "crust" as compared with that of the same leather in the "blue" deserves comment. So far we have found the opposite to obtain in the non-formato chrome tannages. This particular decrease in pH value of the formate chrome tannages is due in all probability to the presence of the stabilizing salt—sodium or calcium formate—the stabilizing salt is present in the leather in the "blue" but not in the leather in the "crust".

It should be stressed that tests 2, 3, 4, and 5 were neutralized during chrome tanning to pH 4.4—somewhat higher than usually obtains in practice (test 1 neutralized to only pH 4.0, a normal procedure in formato-chrome tannage). These data should be interpreted in that light.

A PXX Series of 6 tests was made at the Prime Tanning Company patterned along similar lines to the Q and QR Series just described. The only changes in the pattern were; (1) lime split stock was used, (2) 1.5 per cent calcium formate was used in place of the 2 per cent sodium formate (Q Series), and (3) the final pH value of the chrome liquor (after setting) for the 6 tests was 3.6. The actual procedure of bate, pickle and tan was:

Start with lime split sides in two 5-foot drums (side by side). Run approximately 200 lbs.
Wash 15 mins. at 75°F.
10 mins. at 90°F.
Bate 1% Biobate MS
Run 20 mins.
Stop 10 mins.
Run 10 mins.
Check to faint pink in center (with phenolphthalein)
Wash 10 mins. at 75°F.
Drain
Add 3 gals. water 80°F.
Add 6% salt
Run 5 mins.

Add 1-½% sulfuric acid
2 gals. cold water
Run 30 mins.
When using calcium formate, add 1.5% at this point (without draining)
Run 5 mins.
When adding syntan, add it at this point with all of the chrome in one addition (syntan added to chrome solution just prior to adding to drum).
Chrome tan-7% of 42% basic Tanolin (4% Tanolin KXD plus 3% Tanolin R) dissolved in 8 gals.
Add at 95°F.
Run 2-½ hrs.
Set tan - 63% bicarbonate of soda in 3 gals. at 90°F.
Add in 3 additions - 15/15/60 mins.
Haul, lay overnight on platform, shave, etc.

Experiment	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Number of sides	11 sides	10 sides	11 sides	11 sides	10 sides	11 sides
and weight	203 lbs.	205 lbs.	215 lbs.	206 lbs.	208 lbs.	217 lbs.
Bate	——	——	——	——	——	——
*Pickle	——	——	——	——	——	——
Calcium formate	1-½%	1-½%	none	none	1-½%	1-½%
Tanak AA	none	1-½%	none	1-½%	¾%	3%
Tanolin R	——	——	——	——	——	——
Solution pH						
after 1-½ hrs.	2.8	2.7	——	——	2.95	2.85
after 2-½ hrs.	3.0	2.9	2.4	1.95	——	——
Add bicarb. of soda	.63%	.63%	.63%	1%	1-¼%	1-¾%
**pH–minutes after	(60 mins.	60 mins.	60 mins.	60 mins.	30 mins.	30 mins.
last addition	(3.4	3.2	2.9	3.1	3.75	3.70
Add bicarb.	none	1/4%	1/4%	1/4%	1/8%	1/8%
Run	5 mins.	5 mins.	15 mins.	15 mins.	30 mins.	30 mins.
pH	—	—	3.45	3.35	3.80	3.70
Add bicarb.	1/4%	1/4%	1/8%	1/4%		
Run	20 mins.	20 mins.	20 mins.	20 mins.		
pH	3.8	3.6	3.40	3.55		
Add bicarb.	none	1/4%	1/4%	1/8%		
Run	15 mins.	15 mins.	15 mins.	15 mins.		
pH	3.5	3.75	3.60	3.60		
Add bicarb.	5/16%	3/16%				
Run	20 mins.	20 mins.				
pH	3.6	3.6				
(Total % bicarb. used)	1-3/16%	1-0/16%	1-1/4%	1-5/8%	1-3/8%	1-7/8%

*Solution pH at end of pickle 1.7
**All pH values taken for solutions only.

The 6 tests after tanning were shaved, neutralized, colored, fatliquored and finished into smooth side leather. After finishing the tests were carefully sorted and evaluated. The data relative to sorting are given in Table XV and Figure 37-A.

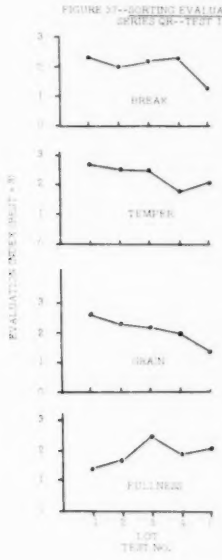


FIGURE 37-A--SORTING EVALUATION INDEX
PXX SERIES--TESTS 1-6

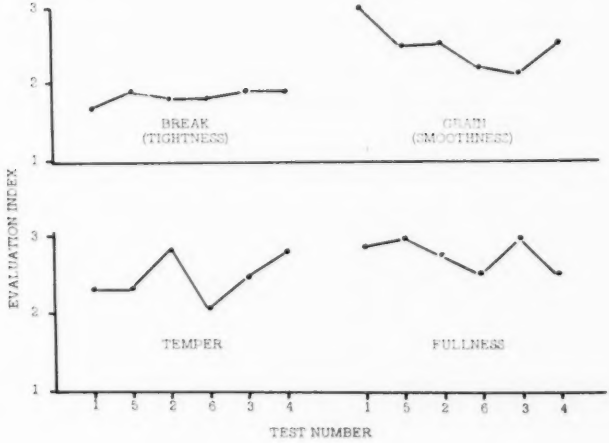


TABLE 15

SORTING EVALUATION INDEX***

	TEST					
	1	2	3	4	5	6
Grain*	3.00	2.56	2.13	2.56	2.50	2.22
Break**	1.67	1.78	1.88	1.89	1.88	1.89
Temper	2.34	2.89	2.50	2.78	2.37	2.11
Fullness	2.89	2.77	3.00	2.55	3.00	2.55

*Smoothness
**Tightness
***Optimum value = 3.00 in all cases.

The tannery in question indicated that test 5 of this series gave the best overall character—in line with the evaluation of similar series in other plants. The evaluation chart shown in Figure 37-A indicates this evaluation to be essentially the case; in other words, the addition of 0.5 to 1.0 per cent acid syntan to the formate chrome tannage gives advantageous results.

5—Effect of Acid Naphthalenic Syntan Addition to the Pickle Prior to Chrome Tannage Upon Chrome Tannage—*Series P*

Various manufacturers have advocated the addition of acid naphthalenic syntan to the pickle, claiming a pretannage an aid to chrome tanning. Studies, made in the Lehigh laboratories some ten years ago, indicated that the acid syntans increased the shrinkage temperature of skin and therefore they are capable, in themselves, of some tanning power. In order to determine the effect of the acid naphthalenic syntans, when used with the pickle and prior to the chrome tannage, some 7 pilot plant tests (series P) were made. For these tests, 200 pounds white weight stock were used. An outline of the tests follow:

Test No.	Formate Added	Syntan Added	Final pH**
1	2%	none	4.10
2	2%	1%	3.94
3	none	1%	3.35
5	none	3%	2.92
7	2%	3%	3.68
4	none	0.6%*	3.50
6	none	1.8%*	3.10

*Salt free acid naphthalenic syntan
**Some amount of sodium bicarbonate used in setting the chromium salt—therefore, the varying pH value.

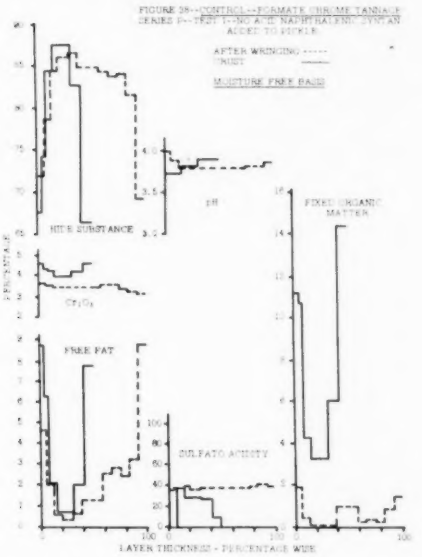
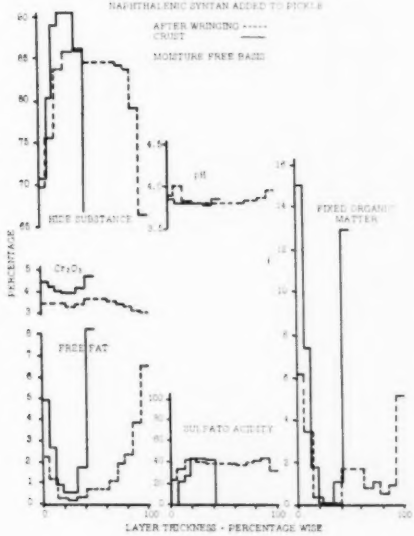


FIGURE 39.—FORMATE CHROME TANNAGE (SERIES I).—TEST 1.—LAYER TEST. ACID-NAPHTHALENE SYNTAN ADDED TO PICKLE



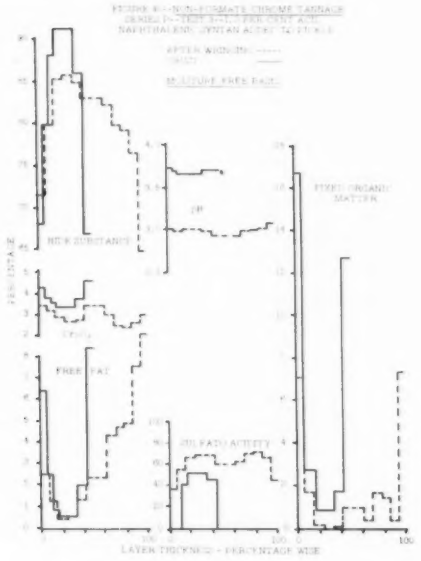
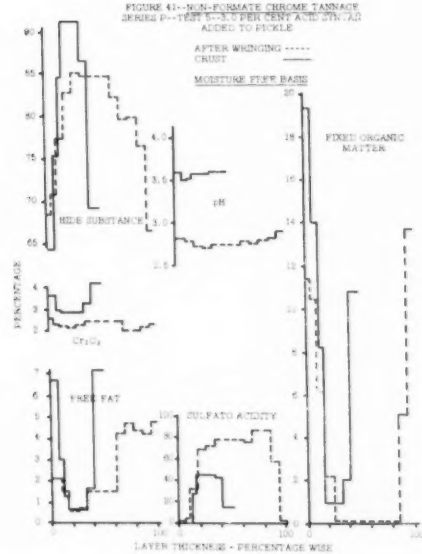


FIGURE 41.--NON-FORMATE CHROME TANNAGE
SERIES P.--TEST 5.--3.0 PER CENT ACID STRAIGHT ADDED TO PICKLE



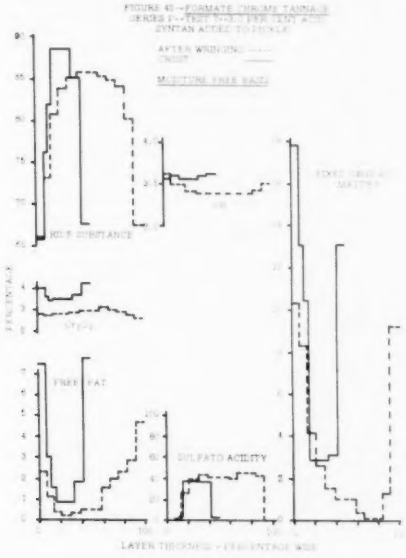
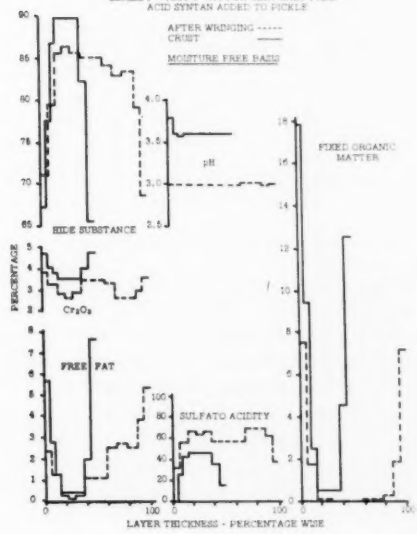


FIGURE 43.—NON-FORMATE CHROME TANNAGE
SERIES P—TEST 4—0.6 PER CENT SALT FREE
ACID SYNTAN ADDED TO PICKLE



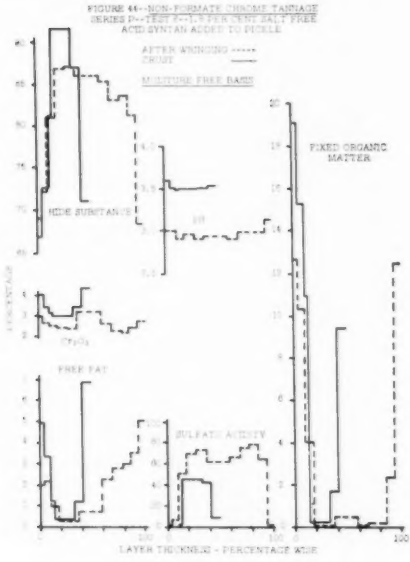


TABLE 16

pH VALUE

Test	After Pickling	After Tanning	After Neutralization	Shrinkage Temperature °C.
1	3.22	3.34	4.10	105
2	3.12	3.25	3.94	102
3	1.20	2.08	3.35	92
5	1.12	1.88	2.92	83
7	2.92	3.10	3.68	95
4	1.20	2.16	3.50	90
6	1.12	2.00	3.10	85

It should be particularly noted that only *one variable* is present, namely, the addition of *acid naphthalenic syntan* and that no attempt was made to establish a constant pH value in the chrome tannage. In this respect, these 7 tests are similar to those already described (Series N) and are therefore, open to the same criticism—in other words, if neutralizing alkali had been added in such amounts as to obtain the same final pH value as the control (pH 4.10), somewhat different leather may have been obtained but in such a case the factual evidence relative to syntan additions would not have been as significant—therefore, only one variable (syntan addition) was used for these studies.

The stratigraphic data, obtained for these 7 tests of the P Series, are given in Figures 38-44. A study of these figures indicates that addition of the acid syntan to the pickle gives a picture somewhat different from that obtaining when the syntan is added with the chrome liquor. There appears to be a somewhat different effect on the Cr_2O_3 fixation in the grain layer when the syntan is used in the pickle in that more Cr_2O_3 is fixed, this is especially true for the non-formato chrome tannages. The reason for this phenomenon may be that since the syntan is used with the pickle, more syntan has penetrated into the skin and gives the skin a "pretannage". For the non-formate tannages, the syntan has a lessened effect on the "sulfato" acidity (for the leather in the "blue"). There also appears to be a lessened take-up of the syntan. The strong stabilizing effect of the formates is shown by comparing Figures 39 and 42 with Figures 40 and 41. Comparing the sulfato acidities and pH values of the leather in the "blue" for the formate versus the non-formate chrome tanned leathers, it can readily be seen that the formate leathers require but little neutralization prior to coloring, etc.

Summarizing, it can be stated that by using the acid naphthalenic syntan in the pickle, less syntan was absorbed or fixed by the skin—this is evident all through this particular series when compared with the N Series. It is apparent that additions of acid syntan to the pickle not only act as *additional acid* but as a partial pretannage. Using acid syntan in the pickle causes the syntan to penetrate and fix with the skin proteins previous to the chrome tannage and thus the same type of chromium compounds may not be formed as when the syntan is added to the chrome liquor and further, the syntan fixation previous to chrome tannage does not allow the full stabilization effect of formato chrome tannage to obtain.

The leather in the finished state was carefully sorted and the following trends were established.

1. In general, the pH and shrinkage temperature values of this series run very close to those of first Series N.
2. The whole series, except for the control, appear to be somewhat firmer and definitely more cracky than Series N. Trends established in Series N appear, in the main, to carry through in this series.
3. This series seems to show less of a "leveling" and "softening" effect from sodium formate. In fact, there is serious question whether the formate has been able to offset the syntan characteristics.
4. There is again evidence that the acid syntan (neutral salts removed) gives a better fullness and break than the straight acid syntan.
5. Tests 1 and 2 (Figures 38 and 39) gave the best leather. In the N Series, Test 2 gave the best leather.

It should be emphasized that the sorting evaluation is for leathers made under the expressed conditions outlined earlier in this report, in which the one variable was syntan concentration with no subsequent modifications such as adjusting the final pH value during tannage or possibly the neutralization prior to coloring or correction in the fat-liquoring operation. These conditions were deliberate so as to make the syntan effects significant. Therefore, the sorting evaluation must be interpreted in this light.

Summary

A careful and comprehensive investigation has been made relative to the use of acid and neutral naphthalenic syntans as adjuncts in the chrome tanning operation. Their use, in the pickle, in the chrome liquor and as setting agents during chrome tanning, has been studied. Summarizing the data from the many tests, it may be stated:

1—No matter whether the syntans are used in the pickle or in the chrome tannage, the syntan anion affects the chromium salt fixed in the leather and in general decreases the fixation of Cr_2O_3 in the grain layer of the skin. This is especially true if the tannage be the non-formate type. If formates are present during the chrome tanning, 0.5 to 1.0 per cent of the syntans has a beneficial effect in that the Cr_2O_3 fixed layer-wise in the skin is practically uniform.

2—The syntan anion replaces sulfato groups of the chromium salt and thus a different type of chromium salt is fixed upon the skin fibers—this can be seen by a study of the "sulfato" acidities of the various test leathers.

3—The presence of syntan appears to redistribute the natural fat present at that time—this is especially true of that natural fat in or near the grain layer.

4—The presence of formates appears to stabilize the syntan-chrome salt and actually give an improved piece of leather—providing the syntan is used in the correct amounts. The presence of formates during the syntan-chrome tannage stabilizes the fixation of Cr_2O_3, pH of the leather and the over-all basicity of the leather.

5—The neutral type of naphthalenic syntan gives a better leather than the acid type. This is shown by a careful study of the data given for Series R.

6—The neutral naphthalenic syntans used in amounts 0.5–2.0 per cent based on white weight and added with the chrome liquor (formates present at the time of tanning), give the best leather, the preference being for the tanneries involved in these studies an addition of 1.0 per cent neutral syntan to the chrome liquor (see Series R).

It should be stressed that a great number of these tests were made in one tannery (Albert Trostel and Sons Company of Milwaukee), namely, Series N,

Q, R, and P, and therefore, the amounts of added syntan may vary from one tannery to another, since beam house treatment, pickling, chrome tanning and many other factors differ from place to place. The data given herein is not to be thought of as a presciption applicable to each and every side leather tannery but to be taken as a trend and, therefore, interesting, practical, and useful if proper interpretation ensues.

ACKNOWLEDGMENT

The writers should like to express their appreciation of the support and encouragement of these investigations given by the American Cyanamid Company, the Mutual Chemical Company of America and the Diamond Alkali Company. In addition, the writers would like to thank the Albert Trostel and Sons Company, the Fred Rueping Leather Company and the Prime Tanning Company, for the use of their pilot plant facilities, for constructive encouragement of the tests involved, for the furnishing of hundreds of sides for the tests, and for the real and valuable sorting of the finished leather, without which the tests would have had little meaning or value.

Received December 29, 1951

Recent Findings on Tanning Properties of Lignosulfonates*

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SUMMARY

Laboratory investigations have been carried out to establish the mechanism of tanning with lignosulfonates prepared by fractional precipitation from spent sulfite liquor, and to determine procedures for using these tanning materials to the best advantage. The sulfonic groups of the lignosulfonates combine with the basic groups of the protein in the hide. The degree of tannage obtainable with lignosulfonates is determined by the pH during tannage and by the amount of sulfonation in the lignosulfonates. Under normal tanning conditions, with pH between 3 and 4.5, 25–30 degree of tannage is obtainable with these fractionated lignosulfonates. By comparison,

*Presented at the Forty-Seventh Annual Meeting, Groton, Conn., June 9, 1951.

the lignosulfonates of untreated spent sulfite liquor yield only 12–17 degree of tannage. This lower tannage is due principally to the higher degree of sulfonation and therefore the lower combining weight of the unfractionated material.

For tanning flesh splits, it was found advantageous to pretan with fractionated lignosulfonates and then to retan with vegetable tan, in order to bring the degree of tannage to the desired level. Depickling is then unnecessary, since the low pH and the salt content are not detrimental to tannage with lignosulfonates, as they penetrate rapidly and are non-astringent.

Tannage with lignosulfonates alone produces stiff and boardy leather—probably due to insufficient cross linkages with peptide groups. In tannage of flesh splits this condition is corrected by use of vegetable tans to complete the tanning action. A similar complementary action is obtained by chrome tannage. Thus chrome tanned leather can be retanned with lignosulfonates and further processed through fatliquoring or stuffing operations to give leather of equal quality to that produced by retanning with vegetable blends.

Introduction

In 1878 the Austrian chemist, Mitscherlich, was granted a patent on a process of digesting oakwood chips with bisulfite solution under pressure, for the purpose of obtaining an extract usable as a tanning material. Independently, the process of cooking wood with bisulfite was also developed by Ekman in Sweden and by Tilghman in the United States, but their interest was in the nearly pure cellulose fibers the digestion gave; thus evolved one of the most important processes for the production of dissolving pulp and paper.

Mitscherlich and many after him have, however, shown that the aqueous extract from the sulfite pulping process does have certain tanning properties. Such extracts in crude or modified form have been and are being sold in large quantities the world over for various uses in tanning processes under various names—for example, Spruce Extract and Totanin (ammonia-base). Among American tanners, this type of material is often referred to as "Sulfite cellulose"—obviously a misnomer since it identifies the part of the wood which the extract does not represent.

The composition of bisulfite extracts of wood (spent sulfite liquor) is fairly well known. The two main components are carbohydrates and lignosulfonates. It is the latter which has the potential tanning value; the carbohydrate fraction is actually useless and lowers tan purity.

Widespread studies during the last twenty years have resulted in better understanding of the nature and utility of lignosulfonates. It has been established that the lignosulfonates in spent sulfite liquors are polymers of propyl-guaiacyl units which vary in degree of polymerization and sulfona-

tion. Increased knowledge of lignosulfonate chemistry makes possible better understanding of the behavior of these compounds in tanning operations. For example, Gustavson[1] has found that the nature of the combination between lignosulfonate and hide substance is primarily an ionic reaction between the sulfonic groups and the basic protein groups. It follows then that more lignosulfonate is taken up by hide substance when the degree of sulfonation is low. Simple salt formation is evidently not the entire explanation for the combination between lignosulfonate and hide substance because the higher molecular weight lignosulfonates combine very firmly with hide substance; in fact, more so than vegetable tans.

The above information indicates that a more valuable tanning material would result by segregating the higher molecular weight, less sulfonated lignosulfonate from the rest of the components of spent sulfite liquor. Such fractionation is technically and economically feasible by controlled precipitation with lime. Through further processing steps, the segregated fraction is converted to a sodium salt with acidity suitably adjusted for tanning.

It is well know that lignosulfonates as tanning agents have several deficiencies which prevent them from being classified as replacement tans. Many procedures and patents describe means of modifying these lignosulfonates, usually by combination with certain chemical groups, to produce a replacement tan. At least so far, the suggested procedures have involved such expensive reaction conditions that the replacement tans, synthesized in this way, would be more costly than the tanning materials they are intended to replace.

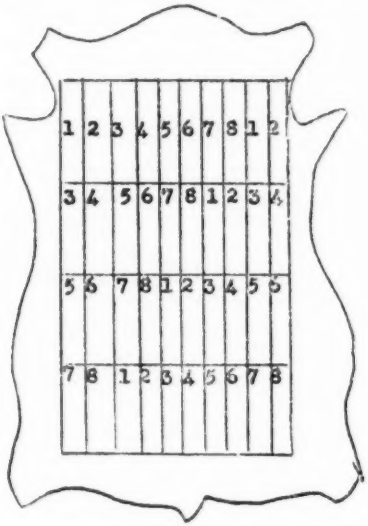
The present investigation establishes practical procedures whereby selected or fractionated lignosulfonates can be used to best advantages as combination tans in various operations. For comparison, an ammonia-base spent sulfite liquor was also evaluated for the same operations. These two products differ appreciably in degree of sulfonation and average molecular weight of lignosulfonate and therefore differ in combining weight. Data on comparative composition are given in Table VII.

Experimental

The present study of tanning action of lignosulfonates was carried out primarily by drum tanning of flesh splits. This type of tannage was selected because (a) the tanning procedures could conveniently be duplicated with small strictly-controlled laboratory equipment, and (b) the raw material could be stored during a reasonable period prior to use so that the experiments did not have to be carried out at or near a tannery. Experimental runs on retanning of chrome tanned leather and the subsequent fat-liquoring or stuffing operations were, however, done at a tannery and in semi- or full-scale operation.

Whole flesh splits obtained in the pickled state were trimmed to remove neck, tail, and belly portions. The remaining hide was then sectioned into 40 pieces, each measuring 4 by 12 inches. Packs were made up containing five pieces each, so selected that the average tensile strength of each pack was the same. These selections were based on strength-pattern diagrams as given by Wilson [2], and numbered as shown in Figure 1. Individual packs were wrapped in moisture-resistant paper and stored at 40°F. until used.

DIAGRAM OF HIDE SHOWING SAMPLE SELECTION



Pack 1 - All pieces marked 1
Pack 2 - " " " 2
Pack 3 - " " " 3
etc.

Fig. No. 1

In the study of tanning flesh splits, the first series of experiments was done by duplicating the customary tannery operation, except that the tan liquors contained various blends of lignosulfonate and vegetable extracts. Thus, the packs of pickled splits were depickled by drumming with sodium acetate, calcium carbonate, and sodium chloride until the pH of the hide was 5 or

above. This operation was followed by washing the depickled hide and tanning in a 3 per cent liquor at 15 r.p.m. at 90°F. Tannage was continued in three volumes of 9 per cent tan, containing fat liquor, at 15 r.p.m. at 110°F., until the splits were struck through and no raw streaks remained. The hides were piled for 24 hours, washed, and tacked to dry. Partially spent liquor from the second drumming was adjusted for concentration and reused for the first drumming of the next load of depickled hides.

In a second series of tests, the depickling operation was omitted and, instead, the pack of pickled hides was drummed with varying amounts of a 10 per cent lignosulfonate solution containing 5 per cent sodium chloride. After complete penetration, the hides were removed from the spent lignosulfonate tan solution and immediately again drummed in a solution containing 10 per cent vegetable tan. The spent tan liquors from each drumming were sewered. This can be done with very small tan loss if, as mentioned later, the correct amount of tan is fed to each drum.

The second series of pretanning and retanning was also carried out using the evaporated ammonia-base spent sulfite liquor as a pretan followed by a 10 per cent vegetable retan operation.

Results and Discussions

The test data on leathers produced by the procedure in the first series are given in Table I.

TABLE I

Tannage of Splits with Fractionated Lignosulfonate—Vegetable Blends

Blend Composition (Tannin Basis)				
Lignosulfonate	0	15	25	40
Vegetable	100	85	75	60
Water Solubles, %	10	10	10	10
Combined Tannin, %	31	32	32	32
Degree Tannage	70	71	71	71
Tensile Strength, Lbs./Sq. In. (Average of 60 tests)	3800	3500	3500	2800

This table shows that tanning of splits with a blend of vegetable tan and lignosulfonate following regular depickling will produce leather with normal properties when the lignosulfonate component in the tan liquor blend ranges up to 15–25 per cent of the total tan. When higher proportions of lignosulfonate are used in the blend, the resulting leather shows lower strength.

Typical data of leathers obtained in the second series are given in Table II.

TABLE II

Tannage of Splits with Fractionated Lignosulfonate Pretan and Quebracho Retan

Pretan	
Combined lignosulfonate, %	17
Degree tannage	24
Retan	
pH	3.5
Moisture, %	10.0
Oil, %	0.2
Insoluble Ash, %	0.3
Water Solubles, %	6.4
Combined Tannin, %	32.8
Degree Tannage	65
Tensile Strength, Lbs./Sq. In.	3100
Stitch Tear, Lbs./In. Thickness	1000

Analysis made according to the American Leather Chemists Association Methods. Stitch tear by Method E.

This table shows that leather of normal composition and strength can be produced by the simple procedure of pretanning pickled hides with lignosulfonate and retanning with a vegetable tan solution. It is, therefore, evident that the depickling step can be omitted. The lignosulfonate part of the tan used is considerably higher than that found permissible when tanning with blends of lignosulfonate and vegetable tans.

The next phase investigated was the effect of the variables in such pretan-retan operation, primarily to find the limits to which lignosulfonate could be used for producing good leather. As illustrated in Table III, lignosulfonate can be firmly combined with the hide substance up to 25 per cent in the pretan operation. If a larger amount is added in the drumming operation, it will not be taken up by the hide under practical pH conditions--namely, in the range between three and four. The degree of tannage obtained with lignosulfonate is therefore limited, the limit determined by the degree of sulfonation. The lower the degree of sulfonation, the greater is the combining weight of the lignosulfonate tanning material. For the high molecular weight lignosulfonate used in the series represented by the data in Table III, the degree of tannage was limited to about 25.

TABLE III

Pretanning Pickled Splits with Varying Amounts of Fractionated Lignosulfonate at pH 3-4

Lignosulfonate added as % on hide substance	29	40	53	91
Lignosulfonate in leather as % on hide substance—				
Water soluble	8	9	13	11
Combined	18	25	24	20
Water solubles as % of total	30	26	35	35
Lignosulfonate utilized, %	90	84	71	34

In a similar series of experimental tannages using the evaporated ammonia-base spent sulfite liquor, the maximum degree of tannage was 15 per cent as shown in Table IV.

TABLE IV

Pretanning Pickled Splits with Evaporated Ammonia Spent Sulfite Liquor at pH 3-4

Lignosulfonate added as % on hide substance	23	35	70
Lignosulfonate in leather as % on hide substance			
Water soluble	8	12	14
Combined	10	10	15
Water solubles as % of total	44	54	48
Lignosulfonates utilized, %	76	63	42

Further additions of tanning material in the pretan drumming do not increase the degree of tannage. The analytical data in Tables III and IV bring out that the amount of water-solubles after pretanning is very low when the high molecular weight lignosulfonate was used, and is higher when the evaporated spent sulfite liquor was the pretan agent. This result evidently reflects the tendency of the low molecular weight lignosulfonates, and possibly other organic acids, to be absorbed but loosely attached by the hide substance, whereas the high molecular lignosulfonate attaches more firmly.

It is thus established that a considerable amount of lignosulfonate, limited by the combining weight of the material used, can be incorporated by the pretanning operation. Such tannage is, however, incomplete and would produce stiff and boardy leather with low shrink temperature and poor re-

sistance to enzymatic action. The lignosulfonate tannage must be complemented by a retannage with vegetable tans to produce leather with all-round satisfactory properties.

The data given in Table V illustrate a considerable range of vegetable retannage. The vegetable tan is taken up readily after the lignosulfonate pretan operation and the tan solution is exhausted rapidly and almost completely. The amount of vegetable tan required for the retan operation depends on the degree of tannage desired in the finished product. As is well known to the tanner, tensile strength decreases as degree of tannage increases.

TABLE V

Vegetable Retannage of Lignosulfonate Pretanned Splits

Degree tannage after pretan	25	20	24
Vegetable tannin added as % on hide substance	14	22	44
Leather composition			
Moisture, %	10	10	10
pH	3.6	3.6	3.6
Oil, %	0.3	0.2	0.4
Insoluble ash, %	0.3	0.2	0.2
Water solubles, %	3.6	4.1	6.4
Combined tannin, %	25.0	24.4	32.8
Degree tannage	41	40	65
Tensile strength, Lbs./Sq. In.	3600	3400	3100

Test data on leathers produced by retanning chromed hides with a vegetable blend containing varying proportions of lignosulfonate are given in Table VI.

TABLE VI

Chrome Retannage—Fat Liquored Leathers

Composition of Tanning Blend			
% Fractionated Lignosulfonate	33	67	100
% Vegetable tannin	67	33	0
Leather Composition			
Moisture, %	10	10	10
pH	3.6	3.6	3.7
Water solubles, %	1.4	2.1	1.7
Ash, %	4.7	3.7	4.7
Cr_2O_3, %	3.3	2.8	3.4
Oil, %	7.5	6.6	7.1
Combined tannin, %	18.2	17.5	16.7
Degree tannage	31	29	28
Stitch tear, Lbs./In. Thickness	1330	1125	1120

Leather properties are as satisfactory with lignosulfonate retan as with vegetable retan. Thus vegetable tans do not have to be present in the retannage of chrome tanned leather if a degree of tannage of 30 or less is sufficient. It is important in order to avoid fat liquoring problems that the lignosulfonate base be monovalent such as sodium. Divalent bases, such as calcium or magnesium result in the breaking of fat-liquor emulsions.

TABLE VII

Composition of Lignosulfonate Products

	(1) Fractionated Lignosulfonate	(2) Evaporated Ammonia-base Spent Sulfite Liquor
Lignosulfonate in product as per cent on solids	73	50
Sulfur in lignosulfonate as per cent on lignin	5.7	9.8
Ratio of combining weight as calculated from sulfonation	1.7	1.0

(1) The fraction of lignosulfonate precipitated when calcium base spent sulfite liquor is treated according to U. S. Patent Reissue 18268 with calcium hydroxide to 11 pH. The precipitate is separated; redissolved and converted to a sodium base of 3.5 pH.

(2) Product obtained by evaporating and drying commercial ammonia base spent sulfite liquor. It includes all the carbohydrate and lignosulfonate originally present in spent sulfite liquor.

Conclusions

Lignosulfonate can be used as a combination tan to replace more expensive vegetable tans, and produces leather with normal physical properties. Larger amounts of lignosulfonate can be used if applied as a pretan, followed by vegetable retan. This procedure has the following advantages: elimination of the depickling step, rapid and even tannage, and nearly complete utilization of the tanning agent.

The degree of sulfonation and the molecular weight of the lignosulfonate determines the amount and firmness with which it combines with the hide substance. In the practical pH range of 3-4, fractionated high-molecular weight lignosulfonate can be firmly combined to result in a 25-30 degree tannage in the pretan operation, whereas evaporated ammonia-base spent sulfite liquor, similarly used, produces a 10-15 degree tannage.

Chrome tanned leather can be retanned with lignosulfonate, either alone to produce leather with 30 degree tannage or with a blend of lignosulfonate

and vegetable tans when a higher degree of tannage is required. Subsequent fat-liquoring or stuffing operations proceed normally when sodium or other monovalent base lignosulfonate is used. The leather produced has normal composition and physical properties.

References

1. Gustavson, K. H., "Investigations of the Reaction Between Lignosulfonic Acid Compounds and Hide Protein," The Royal Swedish Institute for Engineering Research Proceedings, No. 177 (1944).
2. Wilson, J. A., "Chemistry of Leather Manufacture," 2nd ed., Vol. 2, pp. 1056-1063, New York, Chemical Catalog Co., 1929.

Discussion

L. G. Schultz: It is true that lignin products have been of considerable interest to the tanning industry, especially the heavy leather industry for a long time, but in the time of restrictions and emergency we wish that it were available as a real tanning agent in large quantities.

The study of the problem such as we have had presented to us today necessarily involves some speculation about the mechanism of tanning, and I am sure we are all familiar with the results of the work that Lollar and his coworkers have presented on this subject.

We have carried out some work in our laboratory that has not been published but more or less confirmed the work that Lollar has done indicating that the lignosulfonate seems to combine predominantly in one way only, whereas the true tannins of the natural vegetable tans probably combine in several ways with collagen.

F. Steven: How is the physical appearance of the chrome leather that was retanned? Was the blend lignosulfonate and vegetable tan? How does the complete lignosulfonate compare with straight vegetable retannage as far as physical appearance is concerned?

M. Baum: The physical appearance and other properties of lignosulfonate retanned leather was considered equal to the vegetable retanned leather.

Shu-Tung Tu: I would like to ask a question about shrinkage temperature of lignosulfonate. In our knowledge, quite a few give the leather no shrinkage temperature. Is that true?

Baum: That is entirely true, yes. Lignosulfonates do not increase shrinkage temperature as vegetable tans do. The shrinkage temperature after lignosulfonate tannage ranges between 65 and 70, and, of course, without question lignosulfonate is not a complete tanning agent in itself. It must be complemented either with vegetable tans or, as shown in some of the work, as a chrome retan. In the latter case the chrome takes care of part of the tannage in the same way as the vegetable tannins do.

R. W. HAGUE: Did you intend to get more or less mold resistance in your leather, and also in vegetable liquors, with use of these?

BAUM: We haven't made any direct observations on that. I would say offhand, though, that perhaps not too much difference would be observed.

TU: Well, in experiment I was able to get some sort of lignosulfonate which gave a shrink temperature of about 75 and, of course, that is rather still low.

BAUM: I think 75 is perhaps hitting the upper limit which might be expected on shrinkage temperature for lignosulfonate tannage. Actually, shrinkage temperature does vary some. The range which we found is about 68 to 73 for the straight lignosulfonate.

TU: If you blend with vegetable extract, this shrinkage temperature falls between, say, the 80's. Did you get an average on shrinkage temperature?

BAUM: It approaches the straight vegetable tan shrinkage temperature, rather than an average of the two.

SCHULTZ: A question was asked about the quality of the leather, using lignosulfonate on the chrome leather as retannage. We were rather surprised to hear that it gave the necessary fullness and tightness that is required in upper leather.

Usually we consider that the fullness obtained in retannage with vegetable tannins is characteristic, and that the larger molecules give a tighter and fuller leather. Those that combine to give the greatest weight give the fullest leather. You indicate that you only get a degree of tannage somewhere around 25 at the most with lignosulfonate.

BAUM: Actually that type of leather, chrome retanned, fat liquored leather, has been produced on a commercial basis using 100 per cent lignosulfonate retan, and for all apparent purposes the leather is entirely satisfactory. That is the fat liquored type leather.

SCHULTZ: Do you have an explanation for the lowering of the tensile strength with the use of a higher amount of lignosulfonate?

BAUM: No, we have no explanation for that and from our experiments it did appear that lignosulfonate as a pretan has less effect on tensile strength than when used as a component part of the blend. However, we have no explanation for these findings.

I. C. SOMERVILLE: If you had a mix containing lignosulfonate and vegetable, is there any simple method of analysis that will tell you the proportion of each?

BAUM: We don't know of any simple precise method for this purpose. There are, however, several things that can be done. If the vegetable tan is not sulfited, then sulfur analysis will indicate what proportion of the blend is lignosulfonate. Methoxyl content of the blend may be used as an approxi-

mate measure, since vegetable tans contain only about 1 per cent methoxyl whereas lignin contains 14 per cent.

A clear distinction between lignosulfonate and vegetable content of a blend is not easily accomplished.

Lubricating Properties of Mineral Oils When Used as Replacement for Fatty Oils in Fatliquoring*

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Previous publications [1, 2, 3] have dealt with the performance of various, typical sulfated fatty oils in the fat-liquoring of chrome tanned calfskins. In addition to considering the action of the intact sulfated fatty oils, several of such oils were separated into three groups of components representing the true sulfo oil, the free fatty acid, and the glycerides, and the individual effect of each of these fractions was separately studied. This work emphasized that the true sulfated oil, which was termed the "sulfo oil" and which represents perhaps 15-25 per cent of a commercial sulfated fatty oil, serves merely as an emulsifier and does not contribute to the lubrication of the leather. While only slight differences were shown to exist between the lubricating capacity of the various separated oil fractions, they did indicate that the intact triglyceride was more efficient than any of its partial or complete hydrolytic products. Various sulfated fatty oils produced different degrees of lubrication with the more saturated oils exceeding the unsaturated oils in performance and with vegetable oils being slightly inferior to comparable marine or animal oils.

Mineral oils have been used with sulfated fatty oils in the processing of practically every type of leather and in many instances with entirely satisfactory results. The quantity of raw mineral oil which can be advantageously incorporated into sulfated fatty oils will vary greatly depending upon such factors as tannage, degree of lubrication, or finishing, so it must be obvious that no prescribed formula which would govern the judicious use of mineral oil can be outlined at this point. Suffice is it to point out that the quantity may vary from little or none used in dress kid to the very high percentages which are consumed in work glove split leather. While the addition of mineral oil may be often dictated by economical factors, there is an increasing

*Presented at the International Union of Leather Chemists Societies, London, England, September 10, 1951.

amount of evidence to indicate that the results might also be measured in terms of improved performance. Because of the variables previously mentioned, the results can be expected to vary from tannery to tannery and from one type of leather to another.

There is little information in the literature concerning the use of mineral oil in the fatliquoring of leather. In fact, Schindler [4] in his review of fatliquoring developments from 1929-1937 commented on this paucity of information concerning the use of mineral oils in leather and added that the discredit among certain tanners "is due not to the mineral oil, but to misuse of it." Ptschelin and Rabkina [5] on the basis of extensive experiments employing blends of mineral oils with fatty or vegetable oils, concluded that 40 per cent of mineral oil could be advantageously blended with the fatty oil in fatliquoring chrome calf leather. Das et al, [6] using a light mineral oil in conjuction with sulfated fish oil reported that chromed cowhide could be successfully fatliquored with a 25-35 per cent blend of mineral oil. Balfe has discussed the use of mineral oils as a replacement for fatty oils [7] strictly on the basis of their physical and physical chemical characteristics. It is doubtful, however, that a comparison on this basis would adequately characterize the lubricating properties of a soluble oil while, as Balfe points out, the same principles are more applicable to an oiling off procedure.

In this work, a series of soluble oils were prepared containing a constant ratio of emulsifier to raw oil in which the composition of the raw oil varied stepwise from straight cod oil to all mineral oil. For this purpose, the emulsifying components of a sulfated cod oil were separated and reblended to form a base of high emulsifying capacity which was employed in order to permit the addition of significant quantities of raw oil without danger of oil separation in the emulsions. Then by varying the proportion of added fatty oil (cod) to mineral oil in the raw oil, it was possible to obtain some insight as to the effect of increasing contents of mineral oil while holding constant many of the other significant factors. Only in this approach is it possible to maintain the quantity and character of the emulsifying fraction constant while varying the content of mineral oil in the final fatliquor.

Experimental Procedure

With the exception of the preparation of the soluble oils, the procedure followed in this phase of the investigation has not differed from that employed in other phases of this general study [1]. The method of sampling the chrome calfskin and the fatliquoring and testing procedures have already been described.

The emulsifier represented the sulfo oil and free fatty acid fractionated from a conventional commercial sulfated cod oil of 25 per cent moisture and 3.7 per cent combined SO_3. In this manner, it was possible to obtain maximum control of the character and composition of the free oil in the fatliquor,

which free oil is believed to contribute the bulk of the actual lubrication achieved. To this end, the sulfated cod oil was fractionated by Hart's procedure[8] into the sulfo oil, fatty acid-soap, and neutral oil fractions. The results of this fractionation and the analysis of the separated fractions are recorded in Table I. Equal proportions of the sulfo oil and fatty acid fraction were blended and neutralized with potassium-hydroxide and ammonia to a pH of 7.5. This blend constituted the emulsifier and it will be noted that it was free of any raw oil constituents. To one part of the emulsifier blend, two parts of raw oil, comprising increasing ratios of mineral to fatty oil, were added to constitute the final fatliquoring oil. In this manner, maximum control over the composition of the fatliquoring oil was maintained and it was further possible to completely vary the composition of the raw oil from 100 per cent fatty to 100 per cent mineral oil. This would not have been possible by the use of the intact sulfated cod oil as emulsifier since that oil contained 35 per cent of neutral oil plus a considerable percentage of free fatty acids which previous work has shown can serve almost equally well as a lubricant. It will be noted that this synthetic emulsifier blend was neutralized to an initial pH of 7.5.

TABLE I

FRACTIONATION OF SULFATED COD OIL

	Original Oil	Sulfo Oil Fraction	Fatty Acid Fraction	Neutral Oil Fraction
% of Original Oil	—	12.5	31.4	34.4
Water, %	25.3	12.9	0.0	0.0
Combined SO_3, %	3.7	12.7	0.0	0.0
Total Fatty Matter, %	66.8	67.8	100.0	98.6
Acid Value	—	53.1	116.2	2.2
Saponification Value	—	—	203.8	184.8
Saponifiable Matter, %	—	—	93.5	93.2
Iodine No. of Saponifiable	—	85.3	102.6	119.0

The composition of the experimental fatliquoring blends is recorded in Table II. Also recorded in that table are the pertinent data relating to the fatliquoring operation. The mineral oil referred to was a 100 second (100 Saybolt Universal Seconds at 100°F. viscosity) paraffinic type oil. The raw cod oil was a good commercial grade with a free fatty acid content of 4 per cent and an iodine value of 143.

The percentage of mineral oil in the total raw oil of the fatliquor varied from none in Sample number 1 to 100 per cent in Sample number 6. Taking into account the proportion of emulsifier (33 per cent of the fatliquoring oil) the mineral oil varied from none to 67 per cent of the total soluble oil. The variation in the mineral-fatty oil ratio did not alter the actual viscosity of the raw oil since these two type oils have, within reasonable limits, the same viscosity.

TABLE II

COMPOSITION OF EXPERIMENTAL OILS AND THEIR APPLICATION

Sample	1	2	3	4	5	6
Gms. Wet Chrome Leather	300	300	300	300	300	300
Gms. Oil (Dry Basis)	9.0	9.0	9.0	9.0	9.0	9.0
Composition of Soluble Oil, Wt. %						
% Emulsifier (*)	33	33	33	33	33	33
% Raw Fatty Oil (†)	67	57	47	37	17	0
% Mineral Oil (**)	0	10	20	30	50	67
Ml. Water	600	600	600	600	600	600
Description of Emulsion (‡)	W+C	W+C	W+C	W+C	W-S	W-S
Initial pH	7.3	7.4	7.4	7.5	7.5	7.5
Final pH	5.6	5.7	5.6	5.7	5.7	5.7
Exhaustion of Oil, %	97.3	97.2	96.9	99.0	98.8	98.2

(*) Emulsifier is a 50–50 blend of Sulfo Oil and Free Fatty Acids separated from Sulfated Cod Oil anp neutralized to pH 7.5; blended and added on water-free basis.

(†) Raw Fatty Oil is Raw Cod Oil with Saponification Value of 196 and an Iodine Value of 138.

(**) Mineral Oil is a paraffinic base, acid refined oil with a viscosity of 104 Saybolt seconds at 100°F. and an A.P.I. Gravity of 28.8.

(‡) Emulsions at 1–10 dilution at 120°F. after one hour standing W+C means white plus cream; W-S white and stable (no cream).

As the proportion of mineral oil to total fatliquoring oil increased, the dispersion of the emulsified oil gradually improved from one showing a definite cream to practically no cream with the maximum mineral oil content. This would indicate the easier emulsification of mineral oil as compared to fatty oil since in all instances the quantity and composition of the emulsifier was maintained constant. The data all indicate a uniform control of pH over the range of the experiment as well as a complete exhaustion of the oil by the leather. A greater penetration might be expected with the higher dispersion obtained with oils high in mineral oil content.

Results

In all this preparatory work, precautions were observed to obtain a uniform and a complete takeup of oil from the fatliquor. However, it is obvious that some variations in the oil content of the different individually fatliquored samples would exist in spite of the care exercised in the preparation of the solutions. Since the total oil content is one of the most important factors determining the general character of the fatliquored leather, the necessity of maintaining a uniform oil content in all experimental samples is essential to an intelligent reading of the results.

The results in Table III indicate a satisfactorily uniform take-up of oil was obtained in all samples with a variation of less than 10 per cent between the samples with the highest and lowest total oil content. A slight but definite difference in the combined oil, and, therefore, free oil, existed as evidenced by

the decrease in combined oil which occurred with higher proportions of mineral oil in the fatliquoring oil. It has been the contention, based on previously

TABLE III

OIL DISTRIBUTION IN FATLIQUORED LEATHER BEFORE AND AFTER AGING

Sample	1	2	3	4	5	6
% Mineral Oil	0	10	20	30	50	67
Free Oil, % by Wt.*	4.69	4.49	4.80	4.59	5.18	5.31
Combined Oil, % by Wt.	1.20	1.20	1.33	1.36	1.00	0.94
Total Oil, % by Wt.	5.89	5.69	6.13	5.95	6.18	6.25
% Combined Oil of Total Oil						
Before Aging	20.4	21.2	21.7	22.8	16.2	15.0
After Aging	24.8	24.2	23.6	23.2	17.4	15.9

*Based on dry, oil-free weight of leather.

reported data, that the combined oil results mainly from the combination of the sulfo oil with the chrome leather. Thus it was possible to definitely demonstrate the direct relation between combined oil and sulfo oil content (or combined SO_3 content) and, in general, the relation is so close that it accounts substantially for the combined oil in newly fatliquored leather. Since the quantity and composition of the emulsifier was identical in every instance, this slight decrease in combined oil which developed with high proportions of mineral oil cannot be ascribed to any variations in the concentration of combining groups between the various samples. Two possible explanations exist. One is that certain of the more reactive constituents of the raw fatty oil, such as partially oxidized acids, are contributing a minor percentage to the combined oil content either through polymerization or combination with the chrome-hide complex. As such constituents are replaced with mineral oil, the resultant decrease in combined oil content would be detected. The second is that with increasing mineral oil content, the distribution of oil on the fibers is so altered that the availability of the reactive sulfo groups is reduced. The values for the further increase in combined oil content after aging, which are shown in Table III, would indicate some limited reaction between fatty oil constituents and the leather as the more probable explanation of the two.

Other evidence of this type has been developed. Thus in a fatliquoring system containing no unsaturated linkages in the hydrocarbon chain, such as would be the case with a sulfonated mineral oil, this slow increase in combined oil was noted and could only be attributed to the further combination of sulfonate groups with the leather as the reaction was driven to completion with increasing time and temperature. The increased combined oil content may also result to a marked degree through the use of certain unsaturated

fatty oils. Thus sulfated soya bean [3] gave a combined oil content after aging which exceeded by far that which could be stoichemetrically attributed to the sulfo oil content of the oil. It could have resulted only from the oxidation of the unsaturated linkages and either their direct combination with the leather or their polymerization to yield solvent insoluble resins. The results in Table III indicate a slight increase in combined oil occurred on aging to an extent similar to that previously recorded for cod oil. As in previous instances, the increase was slight. The extent of this further increase in combined oil during aging dropped off with increasing mineral oil content in a slight but definite manner.

There has been ample previous evidence [1] to show that the distribution of oil in the various horizontal divisions of the leather depends on the degree of emulsification and the emulsifier content. As the emulsifier content, and the degree of oil dispersion, decreases, the oil shows a preference to deposit on the flesh or base division and the grain takes up a proportionately lesser percentage of the added oil. This is in line with what would be expected histologically in view of the tight fiber structure of the grain compared to the loose open structure of the flesh. Throughout this work, the emulsifier content was kept constant but since the dispersive properties of raw cod and mineral oil vary, some variation in the degree of dispersion of the various fatliquors was noted. Adjustment to constant emulsification could not have been achieved without varying the emulsifier content which would have obviated one of the most important control factors. Actually, based on close observation of other experiments where the degree of dispersion varied, it is doubted if the variation noted in this experiment was sufficient to contribute to significant differences in deposition of the oil in the leather. Certainly no differences occurred in the first three samples, including 0 to 20 per cent mineral oil, yet the definite trend on distribution was established in this group and carried through to the maximum mineral oil content. It should be noted that in all cases of emulsification, a wide variation in particle size develops and only weighted average figures can be reported. In these experiments the bulk of the emulsified particles in all samples would fall in a fairly close range with a minor percentage of particles representing the extremes in particle size. It is estimated that the range of particle size of samples 1-4 would be covered by a 2 to 17 micron particle size with not more than 10 per cent exceeding 10 microns. It is further estimated that the particle size in samples 5 and 6 ranged from 2 to 10 microns.

The data in Table IV show the distribution of free and combined oil in the various horizontal divisions of the fatliquored leather. As the proportion of mineral oil to total oil in the fatliquor increased progressively in samples 1 to 6, a corresponding greater proportion of the available free oil was deposited in the grain. At the same time, the free oil in the base or flesh division showed a marked decrease while that in the corium division showed a gradual

TABLE IV

DISTRIBUTION OF OIL IN THE VARIOUS HORIZONTAL DIVISIONS EXPRESSED AS PER CENT OF THE TOTAL OIL IN THE LEATHER

Sample	1	2	3	4	5	6
% Mineral Oil	0	10	20	30	50	67
Distribution Free Oil Between:						
Grain	28	31	32	33	34	38
Corium	11	11	12	15	19	21
Base	61	58	56	52	47	41
Distribution Combined Oil Between:						
Grain	37	38	34	40	32	38
Corium	8	9	7	9	9	8
Base	55	53	59	51	59	54

increase which ultimately amounted to almost a 100 per cent increase in the free oil in the corium with all raw mineral oil as compared to raw fatty oil (Sample 6 compared to sample 1). It is not probable that this increase in free oil in the corium is directly associated with the corresponding increase in the grain and that it could possibly be the result of deeper oil penetration through the grain layer. In view of the fine histological structure of the grain, it is doubtful if significant quantities of oil penetrate into the corium from this surface and rather is it believed that the corium penetration results preponderantly from the flesh or base division. Since the viscosities of these free oil fractions were approximately the same in all instances, as was the emulsifier content, the increased oil penetration which resulted could only be ascribed to a gradual decrease in the filming of the oil over the fiber surfaces, that is a lessening of the affinity of the oil for the leather, which resulted with high concentrations of mineral oil. The data do show that this penetration accelerates rapidly with high percentages of raw mineral oil and with equal emphasis they indicate that up to 25 per cent of mineral oil can be employed without upsetting seriously this distribution of oil between the various layers. Again it is important to point out that such results on distribution of oil obtained with calf leather will not necessarily follow with other types of leather, such as sheep where the fiber structure is much more open. It must be obvious, however, that for certain leathers where softness and fatliquor penetration are desirable, that the action of mineral oils in promoting this penetration is of interest. On other type leathers, where excessive softness is objectionable, this characteristic of mineral oil will limit the quantity which may be advantageously employed.

The data in Table IV, relative to the combined oil distribution in the various horizontal divisions, indicate a rather uniform distribution in spite of differences in fatliquor composition. In this respect, they do not follow the free oil distribution and since the combined oil is essentially derived from

emulsifying components which were constant in every instance, this distribution is of marked interest. The theory that the deposition of oil in the leather is followed by its redistribution during drying and mechanical working has been previously advanced [1]. Due to its affinity for the leather fibers, it does not follow that the combined oil would enter into this redistribution process as does the free oil. The comparative data in Table IV tend to substantiate this explanation.

In Table V, the analyses of the free oil extracted from the grain and base divisions are recorded. The results correspond satisfactorily to the original composition of the fatliquoring oil and there is no indication that in spite of the variation in oil penetration which has been ascribed to the greater affinity of the fatty oil for leather fibers, that any separation of the mineral and fatty oil components has been effected during this migration of oil.

TABLE V

ANALYSES OF FREE OIL IN GRAIN AND BASE DIVISIONS

Sample	Mineral Oil %	Oil from Grain		Oil from Base	
		Free Fatty Acids %	Saponifiable Matter %	Free Fatty Acids, %	Saponifiable Matter, %
1	0	19.5	98.9	19.0	100
2	10	——	——	——	——
3	20	15.2	82.8	15.5	83.3
4	30	11.4	68.5	11.4	72.9
5	50	9.6	41.1	7.9	41.2
6	67	7.2	24.2	5.3	28.8

The results of the physical testing of the fatliquored leather samples are recorded in Table VI. Because the tear test gave such wide differences, with variously treated leather, particularly when fatliquored samples are compared with controls, it has been considered a valuable measure of the degree of lubrication obtained. Tensile strength values are generally more difficult to check and they often vary to such a slight degree that they fail to show significant trends. The stretch at break has always proved to be a valuable index of leather character.

TABLE VI

PHYSICAL TESTS ON FATLIQUORED LEATHER

Sample	% Mineral Oil in Fatliquor	Tear in Lbs. / Inch	Tensile Strength Lbs. / Sq. Inch	Stretch at Break, %
1	0	223	3590	45.4
2	10	259	4180	44.6
3	20	255	4280	45.6
4	30	262	4190	44.9
5	50	245	3970	43.1
6	67	251	3880	41.4
Control – No Fatliquor		165	3860	37.7

As in previous reports, the higher tear value obtained with fatliquored leather as compared to the control are readily apparent in Table VI. However, as mineral oil gradually replaces the fatty oil in the raw oil fraction of the soluble oil, a marked increase in the tear strength of the leather occurs and it reaches a maximum in the neighborhood of 30 per cent mineral oil content. However, even at the maximum mineral oil content, where raw fatty oil has been completely replaced, the tear strength remained at a high level. There is, in these results, evidence to show that improvement in tear strength can be achieved through the lubricating capacity of mineral oils and that if the tear strength determination is a criterion of lubricating capacity, as previous work has indicated, then the effectiveness of mineral oils of the proper character compares with that of fatty oils. This does not propose that tear strength is either the sole or the most important factor in determining overall leather quality. It has been pointed out that the tear strength reaches a maximum. Also, accumulated work has indicated that some penetration of the corium by the free oil is essential to strength characteristics. To some measure then the increased strength obtained with mineral oils may result from their increased penetrating capacity. Whether there is a maximum penetration beyond which over lubrication can develop, such that some excess fiber slippage occurs and with it a decrease in ultimate strength, cannot be established from the data but it is not impossible that such an explanation may apply here.

The tensile strength value is less responsive to variations in processing but the results recorded in Table VI indicate that they parallel the trend established in the tear strength data to a very marked degree. The fact that the leather sample possessing no lubrication showed a result in the range and even above certain fatliquored samples would indicate that other factors than the lubricant are primarily concerned in this type of test.

The stretch of the leather at the break in the test for tensile strength is a valuable performance index of the character of leather and it is recognized that the ability of leather to give under tension is improved by proper lubrication. For certain types of leather, this high stretch is desirable while for other types of leather too great a stretch results in the rapid loss in shape of the fabricated article. The data in Table VI indicate that the stretch was maintained with remarkable uniformity up to sample number 4 representing 30 per cent mineral oil in the total fatliquor after which a decrease in the percentage of stretch was obtained. The agreement with the pattern established by the tear strength data appears to be more than a coincidence.

The leather samples were also inspected closely by a visual examination and as the mineral oil content increased, the surfaces, both the grain and flesh, were visibly less oily indicating progressively greater penetration. This effect was particularly noticeable in the higher concentrations of mineral oil. Also the softness of the leather progressively increased, which fact correlates

with the increased penetration which has been discussed. As might be expected, the fullness and roundness decreased in proportion. This is consistent with practical experience and is explained by the analytical data for we know that in producing leather where firmness or body is essential, every effort is made to avoid excessive penetration of oil. On the other hand, with soft leathers such as glove and garment, this high penetration of fatliquor is most desirable. As was stated before, these results must be interpreted in terms of calf leather only and the extent to which they would apply to sheep, horse or kid cannot be accurately stated. Other factors such as total oil content, depth of neutralization, and effect of other types of fatty oils or emulsifiers are all involved so that any attempt to apply them to specific industry problems must take these variables into account. It is the intent here to obtain some measure of the basic lubricating characteristics of mineral oil under controlled conditions. Therefore, the interpretation of the data should be confined to the broad aspects of the problem. It is also important to point out that these results are based on the use of a mineral oil of a viscosity practically identical to that of the fatty oil employed.

Conclusions

The comparative performance of mineral and fatty oils as components of fatliquoring oils has never been reported in publications dealing with leather lubrication. In this work, it was intended to study the effect of a stepwise replacement of raw cod oil in a synthetic sulfated cod oil with a mineral oil. Such studies have included a chemical examination of the deposition of oil in the fatliquored calf leather, a determination of the basic physical characteristics of the leather and an exacting visual examination of the character of the leather.

As a result of these studies, the following generalizations may be outlined:

1. As the proportion of mineral oil is increased in a fatliquoring oil slightly improved emulsive properties result.
2. A high concentration of mineral oil reduces the combined oil content due probably to the less reactive character of mineral oil as compared to cod oil.
3. As the proportion of mineral oil in a fatliquoring oil is increased at the expense of raw fatty oil, the deposition of the free oil in the leather is altered as follows:
   (a) A considerable reduction of the quantity of oil in the base or flesh division is obtained.
   (b) A corresponding increase in the amount of oil deposited in the grain results.
   (c) The quantity of oil which penetrates into the corium increases greatly.

4. As the proportion of mineral oil in the total fatliquoring oil increases, the tear and tensile strength increase at first and then gradually decrease with high proportions of mineral oil.

5. The stretch of the leather decreases with high percentages of mineral oil.

6. Raw mineral oil, as compared to raw cod oil, possesses a greater ability to soften leather. This can be attributed to its greater penetrating capacity.

7. From a strictly lubricating standpoint, mineral oil appears to be as effective as a typical fatty oil such as cod oil. It differs, decidedly, in its manner of distribution which fact is reflected in the physical properties of the processed leather. Its value and effect would depend on the quantity employed and the type of leather being processed.

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ABSTRACTS

The Constitution of Wool Wax. By E. V. Truter. *Quarterly Reviews of the Chemical Society*, **5,** 390 (1951). Until recently the unique complexity of wool wax has defied analysis. It has been quite common for one set of workers to be unable to isolate a component reported on by others. Few attempts, all unsuccessful, have been made to separate and identify individual esters. The usual method of investigation is to hydrolyse and examine the resulting acids and alcohols separately. In this way about 60 per cent of the acids and of the alcohols have been identified. This paper surveys the investigations and summarizes the constituents in the light of present knowledge. Weitkamp (1945) has isolated 32 acids in four groups as depicted below. The alcohol components fall into three groups. The isocholesterols are not true sterols; their complete structures are unknown. Dihydric alcohols are present. Traces of unidentified, low melting point hydrocarbons have been found, which are not adventitious impurities. No single ester has been identified. The wax cannot be built up by random combination of the known acids with the known alcohols and the indications are that diesters of hydroxyacids form a considerable proportion of the total. The acidic and the alcoholic fraction each constitute about 50 per cent of the wax.

ACIDIC FRACTION	Approx. %
n–Acids:	
9 members, decanoic to hexacosanoic	7
iso-acids:	
10 members, 8–methylnonanoic to 26–methyl heptacosanoic	22
anteiso-Acids:	
11 members, 6–methyloctanoic to 28–methyltriacontanoic except 26–methyloctacosanoic	29
Hydroxy-acids:	
2 members, α–hydroxymyristic and α–hydroxypalmitic	7
Unidentified portion:	
unsaturated acids	15
unaccounted for	20
	100

ALCOHOLIC FRACTION	
Aliphatics:	
2 members, n–octadecanol, n–docosanol	3
Sterols:	
3 members, cholesterol	20
dihydrocholesterol	5
cholesta–3:5–dien–7–one	<1
*Iso*cholesterol	
4 members, lanosterol	10
dihydrolanosterol	10
agnosterol	1
dihydrolanosterol	4
Hydrocarbons	<1
Unidentified portion:	
straight-chain alcohols	15
diols	5
unaccounted for	25
	100

C. H. S.

An Improved Leather Dressing. By M. Unwin and B. V. Middleton, *Museums Jour.*, **51**, 69 (1951). The authors recommend the following leather dressing:

Lanolin (anhydrous)	35% w/v
Beeswax	25%
Toluol	20%
*Polyvinyl acetate solution	10%
Potassium lactate solution 7% lactate w/v 0.25% p–nitrophenol w/v	8.5%
Sodium chloride	0.5%
Sodium pyrophosphate	1.0%

The lanolin and beeswax are melted together on the water bath. The polyvinyl acetate solution is added with thorough stirring and then the toluene, the mixture being allowed to regain the temperature of the water bath between the additions. Then the potassium lactate and p-nitrophenol are added and finally the sodium chloride and pyrophosphate. The melt is allowed to cool with frequent stirring. The dressing can be diluted with toluol as desired. P.V.A. is added because under laboratory conditions it appears to form a protective film. The pyrophosphate is incorporated to sequester the iron. The leather can be polished after two hours though two days are needed for all tackiness to disappear. Gilt tooling is unaffected. The dressing can be advantageously used on new leather because the lactate enhances the appearance, especially in the case of leather with a pronounced grain.

*20 parts P.V.A. in 100 ml. alcohol. C. H. S.

An Investigation of Some Factors That Affect the Efficiency of Fungicides on Leather and a Description of a New Test Method. By A. J. Musgrave and J. N. Turner. *J. Soc. Leather Trades Chemists*, **35**, 290 (1951). A simple method of evaluating fungicides was used and improvements made. In this method samples of dressing hide 2 inches by 1 inch were treated. Application of fungicide was made by dipping and dropping. The best method of application seemed to be dropping from a small glass syringe. Time was allowed for the fungicide to penetrate and dry. They were then put into humidors and incubated at 30 degrees C. The dose of fungicide was varied by varying the amount dissolved in a constant amount of solvent thus maintaining a constant amount of solvent in the leather. Satisfactory humidors were made by placing the leather in a small tube (3 in. by 1½ in.) inside large tubes (4 in. by 2 in.) which contained water. The larger tubes were sealed with rubber stoppers or waxed corks. These humidors have complete visibility at all times. The code used for recording mold growth was as shown:

(1) Any small growth on grain; (2) any small growth on flesh; (3) small amount on grain and flesh; (4) most, but not all, of grain only covered; (5) most, but not all, of flesh only covered; (6) half of flesh and half of grain covered; (7) most of flesh and a bit of grain covered; or most of grain and a bit of flesh covered; (8) most of flesh and grain covered; (9) all of one side and most of other covered; (10) all of both sides covered. The time when mold growth was first started was regarded as of great importance. Four humidors were set up with untreated leather. After 7 days mold growth appeared on 2 and on all in 8 days. This was considered satisfactory replication. The chief solvents were cold-test neatsfoot oil, cod oil, absolute and 50 per cent ethyl alcohol, and water. Superficially alcohol appears to be a better solvent than oil. This may be because it evaporates more quickly, leaving more fungicide on the surface, whereas oil carries the fungicide into the leather. A comparison of p-nitrophenol in absolute alcohol and neatsfoot oil showed that, particularly with the alcohol, only the surfaces actually covered were protected. A comparison of the penetration of neatsfoot oil and alcohol showed that the oil penetrated to the middle layer of the leather. The alcohol penetrated only just below the surface. Both these comparisons confirmed the belief that the apparent superiority of alcohol as a solvent arises from its volatility. Comparison of dressing leather treated with 0.1 *N* HCl and other with one per cent sodium bicarbonate resulting in pH averaging 3.86 for the former and 4.96 for the latter showed no appreciable differences when given the same p-nitrophenol treatment. From this it is inferred that differences in pH likely to occur in leather have no appreciable effect on the efficiency of the fungicide. It was found that, in order to ensure presence of mold spores and uniformity of results a pretreatment was necessary. This consisted in incubation in the humidors until the leather was completely covered with mold.

It was then brushed clean and used for testing. Samples were also dusted with mold spores after varying periods of incubation. There was evidence that mold would start growth but, unable to combat the fungicide, disappear again. For example, sample to which 0.23 per cent w/w of p-nitrophenol had been applied soon showed slight mold growth, which eventually disappeared. Although it was dusted with spores on the 171st day, it still showed no mold growth on the 369th day. Waxed corks are preferable to rubber stoppers in the humidors because there was some evidence that the rubber exerted a slight inhibiting action on mold growth. Different parts of the hide, whether belly, flank or backbone, showed no differences in susceptibility. Similarly a variation in porosity had no effect. Mold grew with equal frequency on flesh and grain sides. There were indications that mold grew more extensively on light weight samples even when concentration of neatsfoot oil was adjusted to be proportional to the weight. One experiment suggested that similar results would be obtained whether the leather was catechol or largely pyrogallol tanned. Fungicides studied were six phenyl mercury compounds, the acetate, chloride, nitrate, oleate, stearate and borate. Others were p-nitrophenol, trichlorophenol, octylcresol, cresantol 15, solignum, lauryl pentachlorophenate, mystox L S, mystox L A, and salicyl anilide. Mystox is an emulsion of 25 per cent lauryl pentachlorophenate, L S being alkaline and L A acid. Solignum is believed to be chiefly naphthenate. Cresantol 15 is a mixture of chlorinated and unchlorinated xylenols. Septotan is a phenyl mercurial syntan. The results obtained with all fungicides were tabulated. The final conclusions on potency put p-nitrophenol first. Trichlorophenol, beta naphthol and phenyl mercury chloride are all good. The limited solubility of the last named detracts from its use. Dosages, for the main tests, were 0.01, 0.02, 0.05 and 0.1 per cent w/w per sample. Solutions in oil and water are equally effective, solubility and convenience being the sole factors governing the choice of solvent. Alcoholic fungicides do not spread through the leather as do oily solutions. The apparent superiority of alcohol results from quick evaporation which leaves a heavy deposit of fungicide on the surface. Alcohol solutions should therefore be applied to both sides of the leather. The rigorous pretreatment, described above, obviates the need of sterilization of samples and the use of standard innoculum. R. H. T.

Tests on the Abrasion of Wet Leather. By M. E. Caspari, G. O. Conabere and R. H. Hall. *J. Soc. Leather Trades Chemists*, **35**, 303 (1951). Experiments were designed to answer the following questions: (a) Is there a simple relationship between the rates of wet and dry abrasion of sole leather? (b) Are the abrasion results dependent upon the method of wetting, and if so, what is the best method to employ? (c) Since rates of abrasion must depend upon the nature of the abrasive surface, does it follow that a series of leathers, arranged in order for one abrasive, will follow a parallel order for another? The work also necessitated a study of the possible deterioration of the cutting power of the abrasive surfaces used. Wet abrasions were carried out with a machine similar to that used for dry abrasion but constructed of rust-proof materials and fitted with jets for spraying on the water, as well as an outlet for carrying away the abraded materials. Water flow of 760 c.c. per min. was used. Rates of abrasion were measured in thickness of leather removed per min. The friction between the abrasive surface and the leather (balancing moment) and energy dissipated in abrading away 0.1 c.c. of leather were determined. Abrasives used for both dry and wet tests were: (1) Grade 50 carborundum cloth, (2) Waterproof grade 50 carborundum cloth, (3) Waterproof grade 60 paper, all manufactured by J. Oakley & Sons, Ltd. (4) Waterproof grade 60D Hydro Rurexsil paper manufactured by Durex Abrasives, Ltd. The effects of different methods of wetting for wet abrasion tests were made by (a) samples placed on wet cotton wool over night before test, (b) soaked in water one hour

before test, (c) no wetting before test. Direct comparisons were made between wet and dry abrasion with the abrasive cloths and papers mentioned. It was found that the rates of abrasion under wet conditions are not simply related to the rates obtained with the same leathers under dry conditions. Using one type of wet abrasive paper all leathers except one were found to abrade more rapidly wet than dry. For another type, rates of abrasion for both wet and dry were much slower, and the wet abrasion was slower than the dry. Careful checking proved that this could not be due to rapid deterioration of the abrasive or clogging of the abrasive surface. Microscopical examination showed that the fast cutting abrasive had its crystals with the long axes perpendicular to the paper, while on the slow cutting abrasive they were parallel to the paper. The former probably cut more deeply into the leather, therefore abrading faster. Under wet abrasion the softened leather was penetrated even more deeply, thus enhancing the rapid abrasion. On the other hand the crystals of the slow abrasive tended to slide over the surface without cutting deeply. This sliding over effect is enhanced by the softening of the leather. Hence the slow abrasive cuts even slower wet than dry. The rate of wet abrasion depends only to a slight extent upon the method of wetting. For routine testing, no previous wetting is necessary. For the fast cutting abrasive, friction was greater in wet tests than in dry. For the slow cutting, the reverse was true. In general the energy dissipated (expressed in joules per c.c.) decreases with increasing rate of abrasion. Rates of abrasion were tabulated. A typical comparison between the fast and slow abrasives, in wet abrasion, is 0.61 mm. per min. for the fast and 0.14 for the slow.

R. H. T.

The Water Resistance of "Two-Ply" Leather. By R. G. Mitton and G. R. Nice. *J. Soc. Leather Trades Chemists*, **35**, 313 (1951). Since capillaries near the grain surface of light leather are finer than those in the corium and flesh, grain layers largely determine the resistance to penetration of water. To force water through chrome-tanned upper leather considerable pressure is required, but, if flexed while in contact with water, penetration pressures drop as low as one per cent of those required for stationary leather. When a homogeneous piece of leather is flexed, the layers at and near the convex surface are extended, those at the concave surface are compressed. At the median line there must be a thin layer where dimensions are unaffected by the flexing. Conceivably a two-ply leather, with a grain surface at the median line, might have a very high water resistance. To test this possibility two chrome-tanned calfskins, designated (A) and (B), to which no pigment or finishing coating had been applied, were chosen and similar blocks cut from each hide. Two-ply leather was obtained by cementing parallel blocks of one hide upon the other. They were cemented grain to grain (GG), flesh to flesh (FF), grain of A to flesh of B (GF) and grain of B to flesh of A (FG). The cementing was done by cutting half-inch holes in blotting paper and smearing these frames with rubber latex to serve as the adhesive. When pressed between the leather layers there was complete assurance that most of the leather was free of any impervious cement layer. Results of water penetration showed no differences which could not be accounted for by expected fluctuations in the leather itself. The following mean permeabilities, in mg. per cm.^{2} per hour for a difference of 70 per cent relative humidity at 70 degrees F, were obtained: CG, 17.6; GF, 17.0; FG, 16.6; FF, 16.3.

R. H. T.

Photometric Methods of Tannin Analysis for Black Wattle Tannin. By D. G. Roux. *J. Soc. Leather Trades Chemists*, **35**, 322 (1951). New rapid and reliable methods are needed for estimation of tannins because official methods are tedious and time consuming.

While work is being done to improve official methods, it is doubtful that the hide power method will ever be reduced to a simple rapid technique. Development of other methods more suited to rapid work is a natural result. Vorsatz developed a rapid colorimetric method for pine bark extracts, suitable also to quebracho and other tannins containing catechol groupings. This method (based on the red color developed by action of nitrous acid on the catechol group, intensified by alkali and stabilized by urea) standardized against hide powder determination of a known tannin, showed only 0.3 per cent average variation. A refractive index method, which has been devised, is not satisfactory because of the interference of sugar. Two methods which give satisfactorily accurate results are described in this paper. They are spectrophotometric. One is called the Ultra Violet, the other the Colorimetric method. Organic materials containing resonating structures, such as phenyl, naphthyl, anthryl, carbonyl, azo, nitro and hydrosulfide groups, absorb radiant energy in the ultra violet and visible regions of the spectrum. Aromatic compounds possessing resonance characteristics of the benzene ring show strong absorption in the ultra violet region 250-280 mμ whereas nonresonating structures such as paraffins and some sugars are completely transparent. Spectra of related materials have distinct general properties of that class of compounds. Deviations from Beer's law are less frequently encountered in the ultra violet. Black wattle contains chromophores in the form of phenolic nuclei and gives a broad absorption band with a single peak on a Beckman Model DU Spectrophotometer. Lignin sulfonic acid, quebracho and pine bark extract behave similarly. In wattle the absorption is a function of the phenolic tannin content only, since the "half tans" present are insignificant and sucrose, the only nontan, does not absorb in the visible and ultra violet regions. Black wattle tannin oxidizes readily in the highly dispersed state necessary for the analysis, resulting in increased absorption. This may be avoided in two ways: (a) Keep quite concentrated solutions, from 2 gr. per liter to full analytical strength of 6.5 gr. per liter, well stoppered to avoid entrance of air and make rapid measurement as soon as dilution for determination is made. The oxidation of the strong solution by the small amount of air originally present is very slight and rapid manipulation does not give time for much further oxidation while the analysis is being carried out. (b) Using the relatively stable well stoppered solution described in (a), dilute 25 ml. to 1000 ml. as before, but the 25 ml. is pipetted into a flask containing 500 ml. of 0.2 per cent sodium bisulfite. When made up to the mark the resulting 0.1 per cent bisulfite keeps the tannin satisfactorily stable. A carefully prepared black wattle solution was made for standardization and five duplicate determinations of the tannin content made by the hide powder method. Comparison of the absorption density with water was not satisfactory. A zero point standard for comparison consisting of 0.84 gr. benzoic acid per 2 liters, diluted 200/1000 ml., proved to be an excellent and reliable standard. The diluted solution showed an absorption density of 0.434, at 280 mμ and slit width 1.9, against water. Five solutions of the above described tannin sample were made, increasing in concentration from 2.1 to 2.5 gr. per liter by 0.10 gr. amounts. These were diluted 40 times by accurately pipetting 25 ml. of each into liter flasks, each containing 500 ml. of exactly 0.2 per cent sodium bisulfite and diluting to the mark. The Beckman spectrophotometer was set against the benzoic acid standard at 280 mμ and 1.9 mm. slit and the absorption densities of the tannin solutions determined in the usual way. Plotted on graph paper, a straight line relationship between concentration and absorption density was obtained. This is the graph used for the unknowns. The unknowns were made up similarly to the wattle for the standard, the absorption densities determined against the benzoic acid standard as before and their value in terms of tannin content read directly from the graph. Agreement with hide powder determinations of the same solutions was very close. Considering the colorimetric method, the author has shown in a previous chromatographic study, that the bulk of the polyhydroxyphenolic fraction of black wattle extract contains ortho dihydroxy– and ortho trihydroxyphenolic bodies. Only one meta hydroxyphenol, pos-

sibly a phloroglucinol derivative, could be detected and was present in exceedingly low concentration. Colorimetric estimation of such groups has been made by several investigators using ferrous tartrate in the presence of a buffer. The blue violet complex formed is a very delicate test for phenols of this class. The color density varies with the pH, but maintains an even maximum over the pH range of 6.5 to 8.5 with black wattle tannin. It is essential to buffer within this range. In this photometric study a Beckman Model DU Spectrophotometer and the same principles employed with the ultra violet method were used. The ferrous tartrate reagent consisted of one gr. C.P. ferrous sulfate and 5 gr. C.P. Rochelle salt per liter. The solution was unstable and was freshly prepared every 3-4 hours. For the buffer a 10 per cent solution of ammonium acetate, filtered before use, was prepared. The optical density of each new batch of distilled water was matched with that previously used. To get the right conditions for the complex formation the correct amounts of ingredients must be mixed in the right order. To accomplish this 10 ml. of the tannin solution, containing 2 gr. of extract per liter was carefully pipetted to a clean flask. To this was added, in the order named, 120 ml. water, 50 ml. ferrous tartrate reagent and 20 ml. ammonium acetate buffer. The ferrous tartrate-orthodihydroxyphenolic complexes are visually identical for pyrogallol, catechol and their derivatives. Color density differs for the pyrogallol and catechol derivatives but both show the same broad absorption bands with peak at about 545 mμ. This peak is most sensitive to concentration changes and all measurement was therefore carried out at the above wave length. For a zero point standard Thomson's gray solution was eminently suitable. It consists of: $Cr_2(SO_4)_3$–K_2SO_4 24 H_2O—16.67 gr.; Cu SO_4 $5H_2O$—33.33 gr.; $COSO_4$ $(NH_4)_2$ SO_4–$6H_2O$—39.5 gr.; $K_2Cr_2O_7$—120 gr. per liter. It may be used only after aging six weeks, when it becomes very stable. It gave an absorption density of 0.434 at 545 mμ and slit width of 0.02 against water. For making the standard curve, eight solutions of previously analyzed black wattle sample (hide powder method) increasing in concentration from 1.75 gr. to 2.10 gr. per liter by 0.05 increments were used. To exactly 10 ml. of each were added, in sequence, 120 ml. of water, 50 ml. ferrous tartrate reagent and 20 ml. ammonium acetate buffer. Absorption densities, taken 2.5–3.5 min. after addition of the ferrous tartrate reagent in a Beckman set with the gray solution at 545 mμ and slit width 0.04 mm. Plotted on graph paper, the results gave a straight line relationship between concentration and absorption density. The absorption densities of unknowns were determined against the gray solution and their values, in terms of tannin content, read directly from the graph. A typical comparison of hide powder, ultra violet and colorimetric methods is: hide powder 33.2, ultra violet 33, colorimetric 33.2 per cent tannin. From the results obtained it appears that both methods offer new, rapid and accurate techniques for tannin estimation. The ultra violet method is preferable from the point of view of simplicity, rapidity and the greater degree of stability of the bisulfite protected tannin. However, the colorimetric method gives equally accurate results and is applicable to photometric apparatus of simpler construction. Photoelectric colorimeters are suitable. Rough estimations may be made with Nessler tubes. R. H. T.

Tannins, Part II. The Complex Nature of Vegetable Tannin Extracts. By K. S. Kirby, E. Knowles and T. White. *J. Soc. Leather Trades Chemists*, **35**, 338 (1951). Natural tannins can be classified into hydrolyzable and condensed types, according to their reactions with mineral acids. Investigations of the hydrolyzable tannins have led to the conclusion that mixtures are responsible for the tanning action. Isolation of crystalline tannins has confirmed the complexity of tanning materials. There have been fewer investigations of condensed tannins. In general the work done has led to the assumption that single tannins, which can be isolated by purification, are present. The concept of the single tannin has been

based on the assumption that purification will result if tannin is adsorbed on hide powder and then recovered by desorption. But it has been shown that, with the exception of tannic acid, desorption is never complete, each tannin leaving a characteristic amount in the collagen. In this laboratory it has been found that mimosa, desorbed from hide powder, is scarcely less complex than the original, as determined by paper chromatology. It seemed of interest to apply paper chromatology to general study of tannins, both as a possible method of characterization and to demonstrate their complexity. While this paper was being written a communication by Hillis [See *This Journal*, **47**, 198 (1952)], with a similar technique, also gave evidence that tannins are complex mixtures, not single tannins capable of isolation by purification. Hence it is impracticable to purify them through separation, using only an analytical figure as a criterion of purity. The Hillis method separates simple fluorescent components satisfactory, but not the polyphenolic tannins. In this study tannin extracts are dissolved in pyridine: water (1:1) or methoxyethanol: water (1:1) to produce 10, 5 and 2 per cent solutions. A small spot, about 7 mm. diameter, of each solution is applied on a line drawn 10 in. from the top of the paper. Four holes are punched in the corners of the paper and the paper placed on an all-glass frame, holding 8 or 9 papers of 27.5 by 27.5 cm. The loaded frame is then placed in a glass tank containing the solvent, the tank is sealed and irrigation carried out by upward chromatography. After the solvent has reached the top, the paper is air dried and examined under ultra violet light. Most tannins give characteristic fluorescent patterns, which in some cases are modified by exposure to ammonia vapor. The solvent mostly used is n–butanol: acetic acid: water (4:1:5). Wet sec-butanol, tert-butanol: water (7:3) and wet tert-amyl alcohol in addition to the original n–butanol: acetic acid: water mixture are also satisfactory solvents. Whatman papers No. 1, 2, 11 and 20 can all be used, choice depending upon the tannin and solvent used. Quebracho, tizera, mallet, myrtan, urunday, algarrobo, guayacan, oakwood, oakbark, spruce and canaigre extracts have given the most characteristic fluorescent pictures. Pictures and diagrams are given. While most fluorescent spots are unidentified, a yellow one at R_f–0.7 of fisetin is shown present in quebracho, algarrobo, mimosa, tizera and valonea. Ellagic acid shows a yellow spot (R_f 0.3–0.4). The phenolic substances present are demonstrated by spraying the paper with various reagents. The best are ammoniacal silver nitrate, 20 ml. of 5 per cent silver nitrate, plus sufficient 10 per cent ammonia to redissolve silver oxide made up to 100 ml., and freshly prepared bis-diazotized benzidine, 6 gr. benzidine hydrochloride plus 14 ml. conc. HCl plus 980 ml. water mixed with two-thirds its volume of 10 per cent sodium nitrate solution. Besides these two, seven other somewhat less sensitive reagents are given. The photographs given show results obtained with 5 and 10 per cent solutions of the tannin on No. 11 Whatman paper with n–butanol, acetic acid, water (or sec–butanol) subsequently spraying with the ammoniacal silver nitrate. After spraying the papers were washed and dried at 25 degrees in the dark. The authors conclude that the n–butanol: acetic acid: water mixture normally gives the best separation of phenolic substances in the hydrolyzable tannins. The components of the hydrolyzable tannins contain carboxylic acid groups which ionize, the ions travelling at a different rate from the undissociated acids. Rate of travel seems to be important. The n–butanol, acetic acid, water mixture travels fastest and gives the least resolution with condensed tannins. Rate of travel also varies with paper used. Sharpness of spots varies considerably from extract to extract, some quite separate and some in trails. Number of spots is important, some appearing best at 10 per cent and others best at lower concentrations. The R_f of spots vary with concentration, the general cause seeming to be the mutual solubilities of components. Gallic acid can easily be detected by this method, provided other components of similar R_f are not preponderant. It is shown to be present in the extracts of chestnut, valonea, myrobalans, sumac, tara, spruce, oakwood, oakbark, quebracho, eucalyptus redunca and commercial tannic acid. Catechin is shown present in Burma cutch and gambier. It may be present in

guayacan and algarrobo, but is almost certainly absent in all the others. There seems to be no simple substance present from which tannins could arise. There is no general overall pattern, characteristic of all extracts. Any single extract can be identified easily by paper chromatology. The importance of this investigation is that it demonstrates clearly the complexity of the extracts and that there seems to be no reason to assume that any single type of chemical structure predominates among the tannins or that the tanning effect is due to any single component or any single type of reaction. Later work has shown that two-way chromatography gives much better separation. Results will be published later. R. H. T.

An Investigation of the Jamet Method for Drying Tannin Residues. By G. E. Boynton. *J. Soc. Leather Trades Chemists*, **35**, 345 (1951). A rapid and accurate method for analysis of tannery liquor is a long felt need. The minimum time for the official method is about 4½ hours. For many extracts it is considerably longer. One half hour can be saved by using metal evaporating dishes. Silver is permissible. The greatest possible saving is in quick drying of the residues. It is claimed that the Jamet oven will give complete drying in about 3 minutes. The oven consists essentially of a steam heated tunnel through which dry, preheated air is drawn over the evaporating dishes. To check the claim a Jamet dryer was made using silica gel as a desiccant. Tests showed incorrect results if standard porcelain dishes were used so stainless steel was substituted. Jamet recommended use of cobalt chloride paper in the air effluent, the change from pink to blue indicating completion of drying. This was found unreliable and a definite drying time was established. For a majority of extracts 10-15 minutes is sufficient. Air flow was set at 115 cm. per second velocity, which changed the air in the dryer every 35 seconds. The oven gave satisfactory drying in 10-15 minutes (as compared to 2-6 hours in an ordinary oven) for mimosa, chestnut, quebracho, mangrove, valonea and a blend of quebracho: myrobalan as 70:30. It did not give satisfactory results with myrobalan, algarobilla, sulfite cellulose and a 1:1 blend of myrobalan and mimosa. The need for including a dryer for the air used was demonstrated. R. H. T.

Acrylic Resins in the Leather Finishing Field. By R. Shaw. *Shoe and Lea. Reporter*, **265**, No. 3, 20 (1952). Methyl acrylate polymerizes to form acrylic resins. Since organic solvent solution of the resin is inconvenient to use, it has been found to be much more practical to make an aqueous emulsion of the monomer and then polymerize. Such emulsions are about as fluid as water even though they may contain 40 per cent or more of the resin. When the emulsion is applied to leather the water is absorbed, leaving a film of resin on the surface of the leather. This forms an excellent base upon which subsequent finishes can be applied and to which they can be firmly attached. Since acrylic resins are thermoplastic, leather coated with them cannot be glazed but it can, however, be smooth plated to advantage. Acrylic resins give a flexible coating which does not chip or scale when the leather is flexed. The resins find application in two principal ways, namely: as a base coat for subsequent nitrocellulose coats. In many cases they are mixed with other materials such as pigment dispersions, thickeners, wax dispersions, and acid dyes. The second way in which acrylic resin dispersions are used is as a component of conventional water or protein finishes. When so used fewer coatings are required. Better adhesion, improved flexibility of the coating and greater resistance to wet rubbing are obtained.

Aniline Finishes, Lacquers and Lacquer Emulsions. By W. Pohl. *Shoe and Lea. Reporter*, **265**, No. 3, 23 (1952). Lacquer finish, saturated with aniline dyes or with lakes, gives the leather a fuller body and more lively appearance yet retains the aniline effect and

satisfactory covering qualities. Lacquer emulsions reduce the risks of resulting brittleness but have the disadvantage of less fastness to wet rubbing. This can be overcome by suitable top dressings. Aniline finishes have an advantage over pigment finishes in that they permit retention of the natural grain effect.

The Determination of Tan and Combining Values. By O. A. Müller. *Das Leder*, **2**, 257 (1951). The tan value (GW, gerbwert) is the amount of tannin in grams taken up by 100 grams of water-free hide substance from a tan liquor of a given concentration within a fixed time. The combining value (BW, bindungswert) is the amount of tannin in grams which is fixed by 100 grams of water-free hide substance under the same conditions but so that it can not be washed out. After determining GW, BW is found by washing the tanned hide powder thoroughly with distilled water then drying it at 100°C. to constant weight. A study was made of the various factors that might influence the determination of and the conditions required for maximum values. The hide material used in the study was full weight calfskin, not just the middle split as is customary when preparing hide powder. After unhairing in a sulfide lime, the skin was washed in running water until neutral to phenolphthalein, then dehydrated with alcohol-acetone and air dried. Three preparations were made: (a) pieces 1 centimeter square, (b) shavings 1 millimeter thick and 2-5 centimeters long, and (c) hide powder made by grinding wet shavings in a meat chopper. The preparations were soaked in running water, brought to pH 5–5.5 with acetic acid, dehydrated with alcohol-acetone, then air dried. The material contained 10-20 per cent of water, was white, not horny, and stable indefinitely. The tanning materials were "superswiss" chestnut wood extract, cold soluble, "crown" quebracho and French oakwood extract used in three per cent solutions after filtering through paper. The method was as follows: Hide material, containing 4 grams of dry matter, was soaked in a given amount of water (for example, 50 ml. including the hide moisture) then the tanning extract solution was added in 4 portions of 0.1, 0.2, 0.3, and 0.4 at intervals of 0, 0.5, 2 and 4 hours for a 24-hour tannage or at intervals of 0, 1, 4 and 10 hours for longer tannages, chloroform being added to the latter to prevent spoilage. During tannage the solutions were shaken frequently at first then once or twice daily. At the end of the tanning period the solution and skin were poured into a filter tube provided with a filter paper disc. 10 ml. of the clear solution was dried to constant weight for determining GW. After draining off the solution with gentle suction the tanned hide substance was washed for 15-20 hours at 18-22°C. with 10 liters of water after which it was dried to constant weight.

$GW = (a-b)100/4$

where a is amount of dry matter in the original extract solution (total volume used) and b is the dry matter in the spent liquor.

BW is the increase in weight of 100 grams of hide material. Powder and shavings gave approximately the same GW values but shavings were preferable because of better filtration. BW was quite dependent on size of the hide material; pieces took up tannin slowly but also gave it up slowly on washing. Addition of the extract to the dry hide material gave low BW values and is never advisable. The extract should be added in 4 portions. Adding it in one portion gave higher GW values although BW was not altered appreciably. The large tannin particles are fixed by the hide when all the extract is added at once, whereas the small tannin particles also have an opportunity to combine when the extract is added in 4 portions. As the time of tanning was increased, from 1 to 42 days, GW increased slightly in dilute float liquors but very little in concentrated liquors. BW increased considerably with time at all concentrations. Maximum GW values were found with from 200 to 250 per cent tannin, on the dry hide basis, but a maximum GW was not found in 70 days as the time of tanning was increased. BW increased but did not reach maxima with either increasing

proportion of tannin or time. The effect of temperature was investigated by tanning portions of hide material for 10 hours at 20°C. then continuing the tannage for 5, 21 or 42 days at either 5° or 35°C. A temperature rise had little effect on GW but increased BW. All three extracts made soft, light-colored leather at low temperatures but dark, hard leather at 35°C. Aging the tanned powder for 21 days before washing increased BW by 3.7–6.7 units. Both GW and BW were greatly increased by acidifying either the liquors or the hide material. The wash water should be at 20°C., 2 per cent and preferably should have a pH of 3.5 obtained with acetic acid.

In general the work shows that the usual 24-hour tannage does not give reliable values for GW and BW with either natural or synthetic tannins. An overall view of tanning ability can not be obtained unless conditions are varied so that one can learn the tannin hide ratio and tanning time required to give maximum GW and BW values. The hide material should be shavings 1 millimeter thick brought to pH 4 with acetic acid then dehydrated with alcohol and acetone. For each determination an amount of hide shavings containing 4 grams of dry matter should be used and should be thoroughly soaked (preferably overnight) in water before tannin is added. The stock tanning solution should contain 4 per cent tannin and be filtered cold before use. Tan with 200, 300 and 400 per cent (on dry hide basis) of tannin, adding it in portions of 20, 40, 60, 80, 100 and 100 ml. at intervals of 0, 1, 4, 10, 24 and 48 hours respectively. The pH of syntans should be adjusted to 3.5. Stock vegetable tanning liquors must not be adjusted but adjustment may be made during tanning. Tan portions for 3, 10, 21 and 42 days. Washing (for BW) should be at 20°C for 30-40 hours with 20 liters of water. GW is yield based on water and fat-free hide, that is absolute yield, and BW is absolute degree of tannage. I. D. C.

Enzyme Unhairing. By O. Grimm. *Das Leder*, **2**, 265 (1951). Enzyme unhairing is reviewed. This unhairing, according to our present knowledge, depends on the action of proteolytic enzymes on the lower layers of the epidermis. The true hide fiber substance is not attacked. Leather quality may require an alkaline swelling, either before or after loosening of the hair. I. D. C.

PATENTS

Method of Producing Products of Animal Fibers. U. S. Pat. 2570,447. J. W. Hall. Elwyn, J. P. Hollihan, Jr., Garden City, and F. F. Morehead, West Chester, Pa., assignors to American Viscose Corp. Appl. Nov. 24, 1945. A method for manufacturing products comprising fibers which occur naturally in beef tendons which comprises cutting the fibers to a selectively controlled length in the range from 0.1 to 5.0 mm., suspending the cut fibers in a swelling liquid, and forming the suspension into products of a predetermined shape.

Leather Sanding Machine. U. S. Pat. 2.573,936. H. Thede, Sheboygan, Wis., assignor to Armour and Co., Chicago. Appl. Feb. 2, 1949. In a leather-treating machine having a driven cylinder equipped with an abrasive sheet and a resilient roll for urging a leather strip against said abrasive sheet, an air jet pipe mounted for reciprocation in front of said cylinder and provided with spaced openings, means for reciprocating said pipe, and slotted means associated with said pipe opening for directing horizontally-aligned fan-shaped streams of air toward the abrasive sheet of said cylinder.

Process for Extracting Gelatin and Glue. U. S. Pat. 2,575,551. R. E. A. J. Frechin, Darnac, France. Appl. June 7, 1948. In the production of gelatin products, the steps of continuously passing skin shreds countercurrently with a hot aqueous agent adapted to hydrolyze the collagen in said shreds to gelatin and to extract the gelatin so formed through an elongated extraction zone; maintaining a gradient of rising pressure in said zone from an end thereof to an intermediate portion of the same and a gradient of falling pressure from said intermediate portion to the other end of said zone; continuously supplying heat to said zone; continuously withdrawing a portion of said extracting agent from said zone at a point between the point of ingress and said agent into said intermediate portion of said zone and the shred exit end of said zone and withdrawing the remainder of said extracting agent from said shred entrance end of said zone.

Tanning of Hides and Skins with Formals. U. S. Pat. 2,577,033. R. C. Putnam, Marblehead, Mass., assignor to United Shoe Machinery Corp. Appl. March 5, 1948. The method of tanning hides which comprises drying the hide by immersing the hide in a water miscible inert organic volatile solvent, then removing the solvent to obtain a moisture content of from 10 per cent to 15 per cent based on the dry weight of the hides and immersing the hides in a solution containing an inert organic solvent, from 0.3 per cent to 4 per cent by volume of a concentrated aqueous solution of a strong mineral acid, and at least 2 per cent by volume of a formal having the formula

wherein R is an aliphatic radical containing more than one carbon atom, the formal being present in the ratio of from 5 to 15 parts by volume to 1 part by volume of the acid.

Tanning Agents and Process of Preparing Them. U. S. Pat. 2,579,216. C. N. J. Thomsen, Tannus, Germany, assignor to Farbwerke Hoechst, Frankfort, Germany. Appl. May 13, 1949. The products obtained by sulfonating a mixture of colophony and a naphthol at elevated temperatures, reacting a phenol alcohol with the product thus obtained and then causing formaldehyde to act at temperatures of about 90–100°C. upon the condensation product thus obtained, said products showing good tanning properties even at high pH values.

Divinyl Sulfone Tanned Proteins. U. S. Pat. 2,579,871. D. L. Schoene, Naugatuck, Conn., assignor to United States Rubber Co., New York. Appl. June 9, 1949. A method of treating wool which comprises reacting the protein thereof with divinyl sulfone in the presence of an alkaline catalyst.

Leather Softening Adhesive. U. S. Pat. 2,580,167. T. Gelinas, Rochester, N. H., assignor to Hubbard Shoe Co., Rochester, N. H. Appl. March 23, 1950. A leather softening adhesive material comprising natural latex, propyl alcohol, and sulfonated castor oil having from 18 to 30 per cent by weight of natural rubber solids, from 2 to 18 per cent by weight of propyl alcohol and about 0.8 per cent by weight of sulfonated castor oil.

Process for Preparing Chrome Tanning Material. U. S. Pat. 2,580,417. R. P. Follett, Needham, and W. J. Murray, Dedham, Mass., assignors to Arthur D. Little, Inc., Cambridge, Mass. Appl. August 10, 1950. The process of simultaneously preparing a tanning material and valuable by-product organic acids which includes contacting a hexavalent chromium compound with sulfuric acid in the ratio of one mol of chromium compound to about three mols of acid, and treating the resultant product with unsaturated organic acids capable of yielding primary oxidation products stable in the environment of oxidation, simultaneously and mutually oxidizing and reducing said organic acids and said bichromate to yield basic chromic sulfate, drying the reaction mass of substantially all of the water contained therein, and separating said basic chromic sulfate from said dried product.

Treated Fur Fibers. U. S. Pat. 2,581,296. G. M. Rickus and S. G. Hoffman, Norwalk, Conn., assignors to Hat Corp. of America, Norwalk, Conn. Appl. August 4, 1947. In the method of making a dyed fur felt hat body, the steps of mixing inferior fur and entire; depositing the mixture on a cone to form a bat; hardening the bat of the mixed fibers; applying to the bat after hardening and before completing the felting of the fibers a reaction mixture including melamine and formaldehyde and drying said fibers to form a surface of water insoluble melamine-formaldehyde reaction product on the fibers in the bat to improve both the dyeing and felting properties thereof; completing the felting of the fibers and shrinking of the bat into a hat body; and dyeing the felted fabric with an acid dye.

Composition for Carroting Fur and the Like. U. S. Pat. 2,582,086. H. T. Tucker, Scarsdale, N. Y., and R. J. Trimpert, Newtown, Conn., assignors to Frank H. Lee Co., Danbury, Conn. Appl. December 23, 1949. As a composition of matter for the carroting of fur or the like, an aqueous carroting solution containing a non-hydrolyzing oxidizing agent, a volatile hydrolyzing acid, and an acid of the group consisting of phosphotungstic acid and phosphomolybdic acid as a catalyst, said solution having the proportions of 1.0–4.5 per cent by weight said hydrolyzing acid, 3-5 per cent by weight said oxidizing agent, and 0.1–0.4 per cent by weight of said latter acid or acids.

Process for Dyeing Only the Flesh Side of Chrome-Tanned Fur Skins. U. S. Pat. 2,583,269. E. Lüscher and A. Engeloch, Basel, Switzerland, assignors to Sandoz A. G., Basel, Switzerland. Appl. August 30, 1948. In a process of dyeing a chrome tanned fur skin with reserve of the fur, the flesh side only being dyed, the step of dyeing the chrome tanned fur skin with a substantive dyestuff in an aqueous solution containing a capillary active substance selected from the group consisting of soap, oleic methyltauride, the oleic ester of hydroxyethanesulfonic acid, glycerolmonooleate ester sulfonate and lauryl alcohol sulfonate at a temperature of 40 to 50°C. whereby the fur remains undyed while the flesh side is dyed.

Acrolein and Sulfur Halide Process to Strengthen Protein Fibers. U. S. Pat. 2,583,574. H. W. Jones, Berkeley, W. J. Thorsen, Napa, and H. P. Lundgren, Berkeley, Cal., assignors to United States of America. Appl. August 30, 1949. A process for the chemical modification of protein fibers which comprises impregnating the fiber with an aqueous solution of acrolein having a concentration from about 20 per cent to saturation at a temperature from about 4°C. to about 120°C. to chemically combine acrolein with the fiber, washing and drying the fiber, then impregnating it with a solution of sulfur halide in an inert, organic solvent at a temperature from about 20°C. to about 120°C.

Leather Splitting Method and Apparatus. U. S. Pat. 2,583,924. G. R. Baumeister, Boston, Mass., assignor to Lacine Mfg. Co., Cambridge, Mass. Appl. Nov. 4, 1949. An improved leather skiving machine comprising a frame, a skiving knife in the frame, a pair of feed rolls arranged to advance a leather blank against the knife, independently driven means for oscillating one of the rolls in an axial direction, and means for operatively connecting the other roll thereto.

Method of Preparing Solutions of Gelatin in Polyhydric Alcohols. U. S. Pat. 2,584,307. L. F. Tice, Salem, N. J., assignor to Gelatin Research Society of America, New York. Appl. Nov. 24, 1950. An improved method of preparing solutions of gelatin in polyhydric alcohols comprising chilling granulated gelatin and a polyhydric alcohol to about 0°C., adding the gelatin to the polyhydric alcohol, allowing the mixture to stand at a temperature in the range of —5°C. to 5°C. until the gelatin is thoroughly wetted with the alcohol, subsequently heating the mixture at approximately 80–100°C. until a clear, homogeneous liquid is obtained and thereafter cooling the liquid until a solid mass is obtained.

Proofing Permeable Materials. Brit. Pat. 609,486. R. M. Hughes. May 31, 1945. Textiles, feathers, wool, hair, pelts, skins, wood, paper, leather, etc., including articles thereof such as fabrics, yarn, clothes, and linen are proofed against insects by treatment with a composition containing an ether of the formula R–(O-CHCl-CCl_3)n, wherein R means an aliphatic, cycloaliphatic, araliphatic, or hetero-cyclic radical which may be unsaturated or substituted. The ether may be admixed with say bentonite, bole, chalk, kieselguhr, talk, powdered cork or sawdust with or without a dispersing agent to form a wettable powder for a liquid spray, or may be dissolved in an inert high boiling organic liquid such as mineral or vegetable oil, e.g., kerosene, or it may be formed into a suspension or emulsion or concentrate ready to form an emulsion. Thus the ether may be dissolved in say a mineral or vegetable oil, tetrachlorethane, methylhexaline, tetrahydronapharalene, or ethylene dichloride to which an emulsifying agent is added; or it may be dissolved in the emulsifying agent itself. Emulsifying agents specified are soaps, turkey red oils, quaternary ammonium salts, sulphonated fatty alcohols and saponified colophony. Other substances such as phthalonitrile, thiourea or thiourea derivatives, thianthrene, sulphur, copper compounds, nicotine, rotenone, and pyrethrum extract may be present, as well as stickers, e.g., casein, fatty acid salts, rosin and glue, and spreaders and dustbinding agents. The ether may also be dissolved in a liquid which normally boils below room temperature. Inert organic carrier liquids may also be present.

Ornamenting Leather. Brit. Pat. 610,550. Bolton Leathers and F. Hausmann. Jan. 18, 1946. Leather for use in the manufacture of shoes, handbags, etc., is prepared by printing a pattern on the flesh side whereby the interior of the article has an ornamental appearance and the necessity for a lining is avoided. In an example, the flesh side of chrome tanned leather is buffed, brushed and then printed in a rotary machine.

Waterproofing. Brit. Pat. 612,125. J. G. Fife. March 29, 1946. Solid materials normally wetted by water, e.g., cotton, rayon, cellulose esters, leather and wool, are rendered

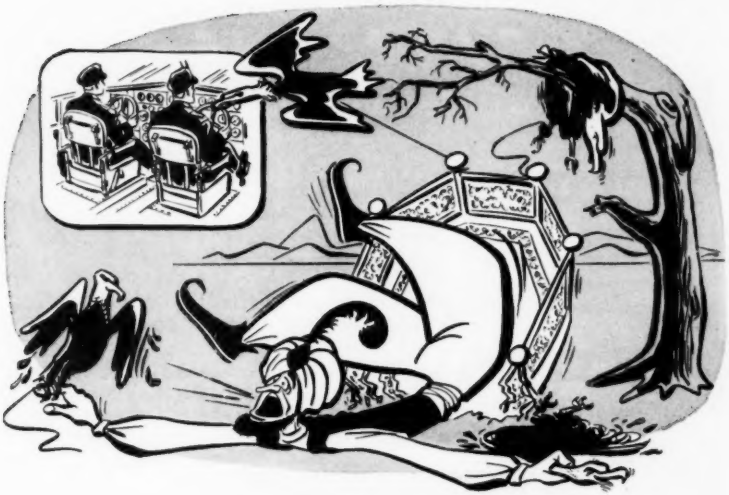
water repellent by treatment with organo-silicon compounds of the general formula

$$(RO)_n R'_{n'} SiX_{4-(n+n')},$$

wherein R represents the same or different hydrocarbon radicals, at least one of which is an alkyl radical containing 8 or more carbon atoms, R^1 is a hydrocarbon or a hydrocarbonoxy radical, X is halogen, and n and n^1 are whole numbers having a sum not greater than 3, n being from 1 to 3 and n^1 from 0 to 2. A number of compounds are specified. They may be applied in a concentrated form or as a solution in an organic diluent, e.g., benzene, toluene or carbon tetrachloride. In example 2, cotton broadcloth is treated with a solution of tri-lauryloxy monochloride in ethylene and propylene chlorides.

Treating Leather. Brit. Pat. 612,372. British Leather Manufacturers Research Association and A. T. Hough. May 22, 1946. Vegetable-tanned leather is treated before, during, or after tanning with an aqueous solution of an amino resin containing boric acid or a water soluble borate; alternatively the treatment may be with two solutions, one containing the resin and the other the boric acid or borate. Suitable amino resins are methylol ureas, methylol melamines, resins derived from toluene sulphonamide and formaldehyde, and polyamides. Hexamethylene tetramine, guanidine, and other nitrogenous bases may also be present. Excess tannins are precipitated, and the wearing qualities of the leather and its resistance to acid rot are improved.

Tanning Agents. Brit. Pat. 615,190. Geigy Akt. Ges. Aug. 2, 1945. Resinous condensates having a tanning action are prepared by condensing a sulphonic acid of a compound of the diphenyl series with formaldehyle and an unsulphonated diaryl sulphone containing at least one phenolic hydroxyl group. The sulphonic acid or the sulphone or both may be precondensed with formaldehyde and then reacted with the other component with or without further addition of formaldehyde. Lists of sulphonic acids and sulphones which may be employed are given in the Specification. The sulphones and sulphonic acid may be produced in situ by reacting a diphenyl sulphonic acid with a quantity of an aromatic oxy compound insufficient for complete conversion into sulphone, e.g., by reacting diphenyl sulphonic acid with phenol to give a mixture of diphenyl sulphonic acid and oxyphenyl-diphenylyl sulphone, which is then condensed with formaldehyde. The condensation may be carried out in acid or alkaline medium; the condensate produced is neutralized and rendered weakly acid with formic, acetic, lactic or oxalic acid. It also may be obtained in solid form by evaporation, salting out or precipitation with acid.



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